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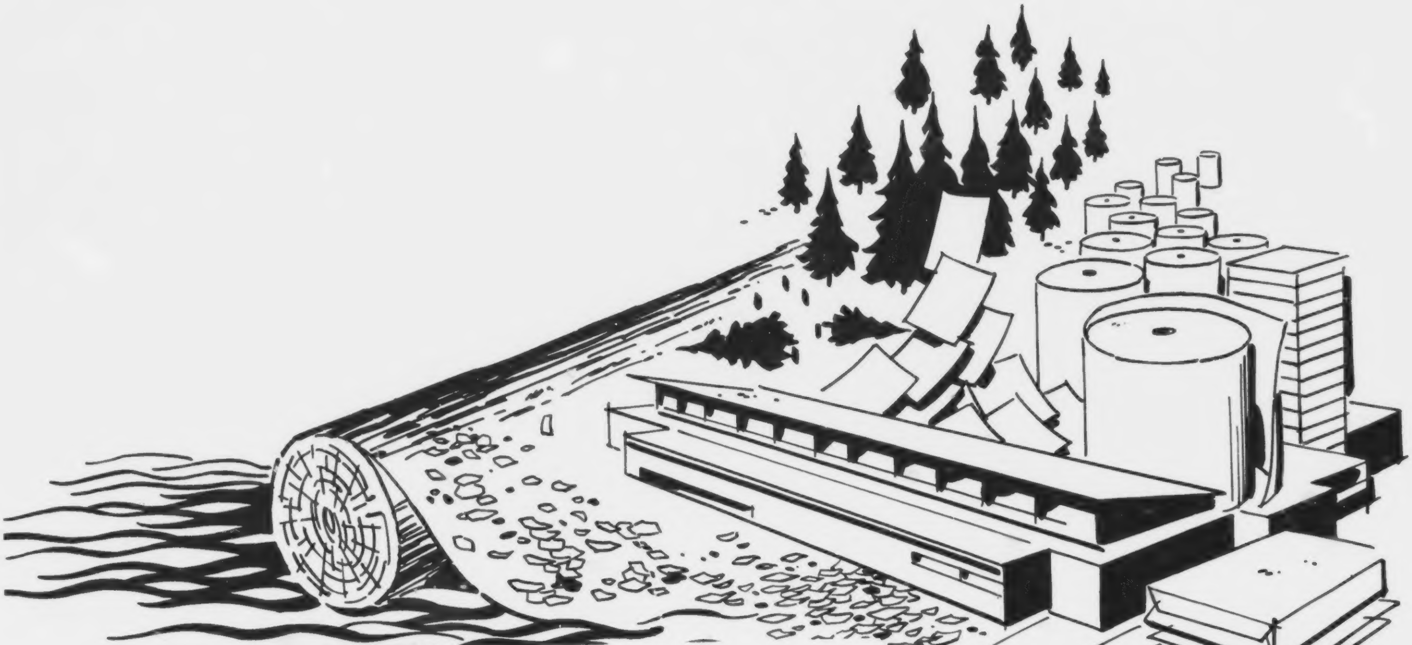

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27 Abstract

Adaptation of reverse osmosis as a method of concentration for dilute effluents of pulping, bleaching, and paper manufacture was conducted in laboratory, pilot scale, and in large 50,000 gallon per day field demonstrations at pulp mills. Most of these dilute wastes at 1 percent solids contained suspended particles, colloidal suspensoids, large molecular-weight wood derived organics, and/or scale-forming inorganic chemical residues. Tubular membrane systems capable of being operated at self-cleaning velocities increasing beyond 2.0 feet per second, as concentration advanced to 10 percent solids, were apparently best adapted to processing these effluents at sustained high flux rates and relatively free of fouling problems. Capillary fiber and spiral wound sheet membrane systems required expensive clarification treatment before and during concentration. Tubular systems studied were subject to excessive failure rates in terms of life of membrane support structures or to leakage of internal connections based on the support structure. Feasibility of employing RO for concentration of dilute pulping and bleaching effluents depends on developing routes to substantial improvement in life expectancy of RO equipment to maintain high flux rates and rejections at much lower membrane maintenance and replacement costs than prevailed with equipment available for these studies conducted from 1967 through 1971.

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REVERSE OSMOSIS CONCENTRATION OF DILUTE PULP & PAPER EFFLUENTS

by

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for the

OFFICE OF RESEARCH AND MONITORING

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ABSTRACT

Adaptation of reverse osmosis as a method of concentration for dilute effluents of pulping, bleaching, and paper manufacture was conducted in laboratory, pilot scale, and in large 50,000 gallon per day field demonstrations at pulp mills. Most of these dilute wastes at 1 percent solids contained suspended particles, colloidal suspensoids, large molecular-weight wood derived organics, and/or scale-forming inorganic chemical residues. Tubular membrane systems capable of being operated at self-cleaning velocities increasing beyond 2.0 feet per second, as concentration advanced to 10 percent solids, were apparently best adapted to processing these effluents at sustained high flux rates and relatively free of fouling problems. Capillary fiber and spiral wound sheet membrane systems required expensive clarification treatment before and during concentration. Tubular systems studied were subject to excessive failure rates in terms of life of membrane support structures or to leakage of internal connections based on the support structure. Feasibility of employing RO for concentration of dilute pulping and bleaching effluents depends on developing routes to substantial improvement in life expectancy of RO equipment to maintain high flux rates and rejections at much lower membrane maintenance and replacement costs than prevailed with equipment available for these studies conducted from 1967 through 1971. This report was submitted in fulfillment of Project Number 12040 EEL, Contract WPRD 02-01-68, under (partial) sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

The capabilities of reverse osmosis as a new tool for concentrating and recovering the solutes in dilute pulp and papermaking effluents have been confirmed in intensive exploratory studies in laboratory and small pilot-scale test programs. Optimum performance was best achieved in concentrating dilute feeds at about 0.5 to 1.5 percent solids by about 10 times to provide concentrates at 8 to 10 percent solids, and with membrane rejections of 90 to 99 percent for most components in the feed. Low molecular weight salts and volatiles were less well rejected.

Problems of concern and for which compensating operation parameters were studied and developed included:

Fouling of the membranes by suspended particles, colloidal suspensoids of large molecular weight organics, resins, pitch and the like could be at least partially controlled by pretreatment, by periodic pressure pulsations believed to achieve backward osmotic flushing through the membrane and by periodic washing of the membrane surfaces. But self cleaning, high velocities of flow were found to be the most likely route to maintaining high rates of flux through the membrane, and especially so with the newer, high performance, tight surface membranes becoming available for field tests in 1971. Minimum velocities of 2 feet per second overcame concentration polarization, but 3.0 feet per second were required to maintain adequate mass transfer rates. Osmotic pressures ranging from 50 to 80 psia in bleach effluents and chemimechanical pulp wash waters fed at 1 percent significantly reduced the effective driving force as concentrations reached 10 percent solids and osmotic pressures of 310 to 330 psia. Higher operating pressures were needed to reach upper levels of concentration in those substrates. Concentration polarization did not appear to seriously affect performance in these studies at operating pressures below 800 psig.

Larger confirming trials were conducted in field demonstrations ranging from 5000 to 50,000 gallons per day on five waste flows of particular concern to the industry. Concentration of the materials suspended or dissolved in these wastes could be achieved at high levels of recovery for all but the smaller molecular weight solutes and volatiles.

However, it was not possible to demonstrate sustained, long-term process operating feasibility in the extended life performance tests of the membrane equipment available for these demonstrations because of the low levels of reliability for available membrane equipment in terms of freedom from plugging of channels, freedom from failure of membrane support structures, and freedom from serious leakages of internal connections within the membrane module. Those capillary fiber and spiral wound sheet membrane systems tested were of excellent structural design and stability but were subject to irreversible plugging by particulate matter contained in the feed or which developed during concentration. Tubular systems operated at high velocities substantially solved plugging and fouling problems, but none of the tested tubular designs were free of structural failure or alternately of internal leakage problems.

Processing economics were affected most importantly by module failures, and the resultant excessive charges for replacement and of maintenance ranged as high as 60 to 80 percent of total operating charges as determined in computer based comparative cost studies.

Engineering studies for optimizing RO design indicate manifolding of half inch diameter tubular systems might best be directed to limiting installations of modules in series to a very few units (250 to 300 linear feet maximum) for each stage of concentration. The number of stages seems of less concern as long as total holding in the system does not exceed limits of about one hour. Hold up in the system should not promote chemical precipitations or aging and break up of colloidal systems, nor should it approach cell regeneration times for microbiological slime growth. Straight-through operation of membrane systems is indicated as a desirable goal with hold-up by recycling and in surge systems limited to minimum periods of time.

Cost evaluations appear most sensitive to membrane module replacement and maintenance charges in terms of sustained performance and life expectancy; to membrane permeation rates as measured by the reference NaCl flux rate; and to increase in osmotic pressures as concentration proceeds. Large-scale commercial applications in the waste treatment field cannot be expected until life performance of membrane equipment has been improved far beyond the less than one year expectancy demonstrated in these trials. Engineering design and manufacturing quality control are problems under intensive development by suppliers and the future of RO will depend on the success of these efforts.

SECTION II

RECOMMENDATIONS

The chief roadblocks delaying practical application of RO to waste treatment problems lie in the several causes for short life expectancy of the membrane system. The less than 12-month life which could be demonstrated in these studies, in terms of either stress fatigue-related failures of the membrane support structures, or alternately of sustained performance, free of module plugging and internal leakage problems, was responsible for excessive operational charges. Module maintenance and replacement charges for short-lived equipment were calculated to range to as much as $2 per thousand gallons of permeate water production.

Suppliers of membrane equipment, all of whom have been straining to perfect module design and manufacturing quality control to increase life expectancy, should be encouraged in every way possible to attain goals of a minimum 3-year average life, and the resultant reduction in maintenance and replacement charges.

Optimization of design of manifolding systems for large installations of RO equipment should be verified with further mill trials under actual plant operating conditions, and with minimum hold-up times, to reduce degradation effects arising from aging of the feed waters.

Membrane development to increase capabilities for operating at wider ranges of pH and temperature could substantially reduce operating charges. Cooling of feed liquors can be a substantial expense, and higher temperatures of operation could reduce or eliminate microbiological sliming. Neutralization to suitable pH ranges for membrane processing can involve substantial expense for reagents, and importantly also may involve chemical or physical changes of phase, such as formation of precipitates or break up of colloidal sols, with resulting fouling problems.

Dynamic membrane studies should be advanced to achieve higher levels of solute rejection without serious reduction in permeation rates. Some waste flows have components, such as lignin, with capabilities for dynamic membrane formation. Development of controlled conditions for formation, removal, and reformation of such supplementary membrane effects could substantially improve performance and cost parameters.

Promotion of turbulence of flows across the membrane surface has been advanced with some success as a method of reducing power costs. Improvements are needed for designs tested in these studies to reduce side effects, and especially of fouling in the presence of turbulence promoters.

SECTION III

INTRODUCTION

An intensive program of screening, evaluating, and adapting of the relatively new developments in membrane processes to the increasingly urgent problems of treating dilute liquid wastes of the pulp and paper industry was initiated in 1958 in the laboratories of the Pulp Manufacturers Research League (located on the campus of The Institute of Paper Chemistry). Electrodialysis was first studied in detail up through substantial pilot-scale studies. Continuing development of other membrane processes in the program of the Office of Saline Water, U.S. Department of Interior, became of increasing interest, and additional League studies on reverse osmosis (RO) and ultrafiltration were activated in 1965.

The first technical paper published in 1967 from these studies adapting RO to the pulp and paper field[1] attracted the attention of Federal pollution control authorities, and it was suggested that the program might advantageously be extended and the development of practical applications be accelerated by partial support from Federal research funding then becoming available. An application to the Federal Water Quality Administration (now the Environmental Protection Agency) was formulated and accepted as Research and Demonstration Grant 12040 EEL for this study on a total budget of $690,530.00, of which 70 percent, $483,370, derived from the Federal grant and the remaining 30 percent, $207,160, was funded by the Research League and individual pulping concerns interested in field studies at their mill sites.

In support of such an application, a field demonstration program was planned and substantial laboratory studies needed for design of field equipment were carried out during the 6-month period of final negotiation for the grant.

Final specifications and contracting for construction of the large trailer-mounted field unit could then be established promptly, after the terms of the grant were finalized September 26, 1967. Final specifications were developed for the field unit; bids were solicited; a contract was negotiated; and final fabrication and assembly completed in time for delivery of the unit October 9, 1968. Start-up tests were completed in about three weeks and the first field demonstration was gotten under way October 31, 1968.

Five field studies (three with the large unit at 50,000 gallons per day and two with smaller field units at 1500 to 8500 gallons per day) were conducted at intervals thereafter on (1) calcium-base acid sulfite "digester cooling water," on (2) Neutral Sulfite Semichemical Machine "White Water," on (3) NH_3-base acid sulfite pulp wash water, on (4) kraft second-stage, alkaline extraction, bleach plant effluent (KBE), and finally on (5) the wash water from a high yield chemimechanical pulping process obtained by screw pressing high density pulp slurries.

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Much laboratory research on special problems and an extensive program of careful analytical control were carried out concurrently on a smaller scale at the mill sites and in the League's central laboratory in Appleton.

Active laboratory and field studies were completed June 30, 1971 and several months have been spent thereafter in collating and evaluating the extensive backlog of data which accumulated during this 4-year research and demonstration study.

The Pulp Manufacturers Research League merged into The Institute of Paper Chemistry effective April 1, 1970, but this research program was continued without interruption by the League staff, which then became the Effluent Processes Group of the Institute's Division of Industrial and Environmental Systems.

These intensely interesting laboratory research and engineering application studies for this membrane process were conducted during a period of great competitive activity among many equipment supply firms each striving to be first on the market with practical membranes and efficiently designed modular membrane support equipment, pumps, controls, and instrumentation as production items ready for commercial-scale use. Development of reliable equipment with desirable life performance expectations has been more difficult than anticipated, and has required years rather than months to attain. Actually, the work reported has been conducted with a series of prototypes undergoing a continuous process of improvement in design, construction, and performance.

Membrane equipment suppliers have supported an amazing and costly program of research and development on new and improved membranes and support structures. No authoritative sources are known on which to establish firm estimates of the total research funding devoted to development of reverse osmosis equipment over the past ten years, but there are guesstimates that costs to industry, university, and governmental laboratories and engineering research centers have ranged to the $100 x 10^6 level. This project has benefited greatly from the extensive interest and cooperation from all of these sources. Commercial application and use of reverse osmosis can be expected much sooner than would otherwise have been possible.

Steady development of the proving out process and the eminent availability of practical RO concentration processing equipment has substantially affected the thinking and planning for environmental engineering studies on industrial waste treatment. New and improved routes to compliance with new and more rigid standards of quality for industrial process effluents are being sought. The availability of reverse osmosis as a new tool for completing the closure of process water systems is developing as another interesting area of application.

The first RO spin-off project directed to closing a pulp mill process water system is under way at the NSSC mill of Green Bay Packaging Inc., the site of the second field demonstration. This has advanced through a first phase evaluation of membrane equipment available on the market as of 1970-71 under a second Research and Demonstration Grant to that company by the Environmental Protection Agency.

A second application research program is in advanced stages of organization on kraft bleach effluent chemical recovery, which is expected to be actively under way at The Institute of Paper Chemistry early in 1972.

Additional application studies are in various stages of planning on other waste streams.

This report is directed to delineation of the areas of possible use for RO concentration processing equipment within the pulp and paper industry. It will be interesting indeed to see the development of pathways and the actual commercial-scale applications which develop within the industry as a result of this pioneering effort.

Importantly, with respect to the identification of the exact source or manufacturer of equipment tested and for which data are reviewed, the reader's understanding is solicited on the format and design of this report.

Every effort has been made to evaluate the advantages inherent in the basic classifications of the many membrane formulations and the wide variety and conformations of modular membrane support structures. Most of the studies were conducted on the cellulose acetate class of membranes, with lesser studies on the nylon product. This report has not been directed to identifying individual formulations (usually proprietary) for diacetate, triacetate, and polyamide products. The studies have covered substantial comparative evaluations of three basic RO design of membrane systems, including the capillary fiber, sheet membrane pack, and tubular conformations. The text avoids identification and discriminatory discussion of proprietary designs under continuing development by individual manufacturers. An exception concerns purchase of equipment with project funds. Such equipment, and particularly that mounted on the trailer field unit, is specifically identified. Equipment was purchased after careful evaluation of its relative merits and advantages at the time of initiating a specific study. Changes and improvements in design have substantially altered the status quo on a month by month basis.

Great monetary benefits to the project arose in the supply without cost of numerous samples and test modules of membranes and equipment for life testing, as described in Section IX. This has often been at substantial cost to the suppliers cooperating in these evaluation and exploratory research studies. This contribution and excellent cooperation is gratefully acknowledged. A list of cooperators is supplied in Section XI.

SECTION IV

PRINCIPLES OF REVERSE OSMOSIS AS APPLIED TO CONCENTRATION PROCESSING OF PULPING EFFLUENTS

Knowledge of osmotic phenomena dates back more than two centuries — the experiments of the Abbé Nollet on diffusion through animal membranes were published in 1748. It was over a hundred years later, however, that experiments with artificially prepared membranes were successful (by Traube in 1867). In 1877 Pfeffer made the first quantitative measurements, using a membrane consisting of copper ferrocyanide precipitated in the pores of porcelain. A good review of early work on osmosis was written by Findlay[2].

This section contains a description of the phenomenon of osmosis, a brief development of the thermodynamic theory, a discussion of concentration polarization and fouling of the membrane, and some general considerations of how these principles will effect the large-scale application of reverse osmosis (RO) for concentrating pulp and paper industry dilute effluents.

Description of Osmosis

Osmosis depends on the existence of a membrane that is selective in the sense that certain components of a solution (ordinarily the solvent) can pass through the membrane, while one or more of the other components cannot do so. Such a selective device is called a semipermeable membrane. When a dilute solution is separated from a concentrated solution by a semipermeable membrane, there will be fluid transfer from the dilute to the concentrated stream until an equilibrium pressure exists on both sides of the membrane. This equilibrium pressure (actually, the equilibrium pressure difference between the solvent and solution phases) is called the "osmotic pressure." Osmotic pressure is a colligative property of the solution and cannot depend in any way on the membrane, so long as the latter has the necessary property of semipermeability.

Application of a positive pressure on the concentrated side of a membrane, equal to the osmotic pressure plus a small, positive differential, will cause the fluid to flow from the concentrate to the dilute stream. This phenomenon is called "reverse osmosis" and the amount of water flowing in the direction opposite to the osmotic flow is directly proportional to the differential pressure applied for any given membrane porosity (Fig. 1).

The performance of a reverse osmosis membrane is generally characterized by the flux rate and rejection capabilities of the membrane. The flux rate at any concentration of the liquor can be related to the osmotic pressure of the liquor by the following equation:

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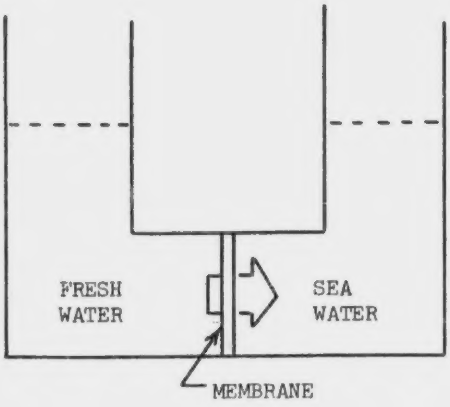
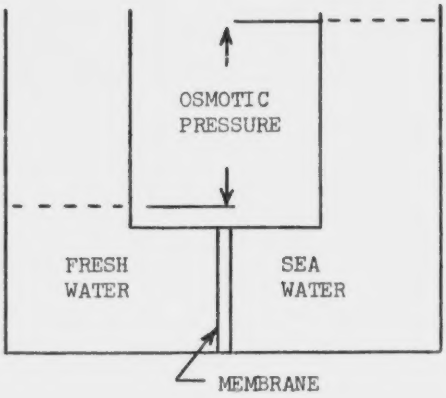
OSMOSIS

When fluids of different concentrations in a vessel are separated by a membrane, the dilute solution will flow through the membrane into the concentrated solution


FRESH
WATER
SEA
WATER
MEMBRANE

OSMOTIC PRESSURE

The level of the dilute solution drops and the level of the concentrated solution rises until an "equilibrium" is reached. The pressure difference between these two levels is the "osmotic pressure."


OSMOTIC
PRESSURE
FRESH
WATER
SEA
WATER
MEMBRANE

REVERSE OSMOSIS

If a pressure in excess of the osmotic pressure is applied to the concentrated solution, the flow is reversed from the concentrated solution to the diluted solution. This is "reverse osmosis."

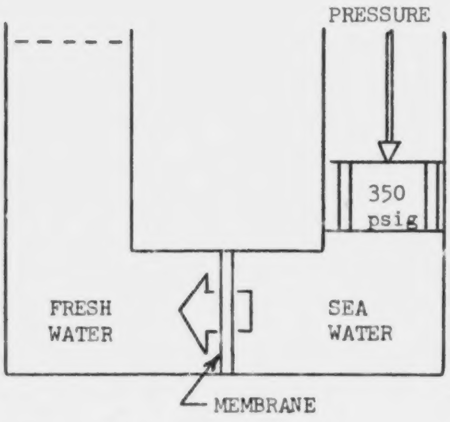

PRESSURE
350
psig
FRESH
WATER
SEA
WATER
MEMBRANE

Figure 1. Schematic Diagram of Reverse Osmosis

$$F = A(\Delta p - \Delta \pi) \qquad (1)$$

where

F = flux rate through the membrane, gfd
A = water permeability coefficient, gfd/psig
Δp = difference between the applied pressure and the delivery pressure of product water, psig
$\Delta \pi$ = (difference between the osmotic pressure of the liquor and product water) + (osmotic pressure increase due to concentration polarization and fouling effects), psig

The product water is delivered at atmospheric pressure. Since the osmotic pressure of the product water is usually very small compared to the osmotic pressure of the liquor, the former term can be ignored. In the case of zero concentration polarization and fouling effects, the driving force ($\Delta p - \Delta \pi$) becomes equal to the difference between the applied pressure (P_A) and the osmotic pressure of the liquor (π). Therefore, equation (1) becomes:

$$F = A(P_A - \pi) \qquad (2)$$

From equation (2), it is apparent that the higher the osmotic pressure of the liquor the lower the flux rate for a fixed applied pressure. The osmotic pressure of a solution depends on the concentration, activity coefficient, degree of ionization of the various components in solution, and the temperature.

In equation (2)

$$\pi = iRTC \qquad (3)$$

where

π = osmotic pressure, atm
i = Vant Hoff's factor, which takes into account the degree of ionization and activity coefficient
R = gas constant = 82.1 atm/g mole cm^3 ^oK
T = temperature, ^oK
C = concentration, g mole/cm^3

For an ideal dilute solution, i has a constant value. Therefore, the osmotic pressure, π, is directly proportional to the temperature and concentration of the solution. In the case of pure water, π is equal to zero.

The rejection ratio is an important parameter in the design of a reverse osmosis unit for the purpose of concentrating the feed over a wide range or for chemical fractionation systems. For membrane concentration processing, the rejection ratio is defined as the ratio between the concentrations at both sides of the membrane at a certain spot:

$$R = (1 - \frac{C_p}{C_f}) \times 100 \qquad (4)$$

where

R = percentage rejection ratio
C_p = concentration of the permeate
C_f = concentration of the feed to the module

It is important to mention here that both of these concentrations should be considered from the standpoint of being measured instantaneously.

Concentration Polarization and Fouling of the Membrane

Most of the dilute wastes of pulp and paper industries are complex in character, containing significant amounts of colloidal and fine particulate suspended solids. These colloidal and suspended solids have a tendency to "coat" or "foul" the membrane surfaces, thus resulting in poorer long-term flux rate and rejection characteristics of the membranes.

Coating or concentration polarization implies the accumulation of solids at the membrane surfaces due to the bulk movement of liquor toward the membrane and rejection of solids at the membrane liquor interface. The solids concentration at the membrane liquor interface increases until back diffusion caused by the concentration difference balances the corrective flow of solution to the membrane and that which leaks through the membrane in the product water. A good review of concentration polarization and its effects on flux rate have been described extensively in the literature[3,4]. Fouling of the membrane surfaces by microbiological growth is often observed in sustained operations with wastes containing nutrients capable of promoting growth of bacteria, yeasts, and molds.

One of the methods of minimizing concentration polarization and fouling of reverse osmosis membranes has been to maintain adequate degrees of turbulence and mixing within the membrane tube. The concept of higher velocity is very useful in sweeping the membrane clean, thus maintaining economically feasible long-term, steady flux rates. However, it should be kept in mind that, although higher velocities across the membrane surface can reduce the physical accumulation of solids near the membrane, they cannot eliminate chemical or electrical affinity which the solids may have with the membrane. Special problems of pretreatment may arise if such affinities are apparent. A detailed description of the effects of velocity on the flux rate and rejection performance of RO membranes is discussed in the later sections of this report.

Application of RO Principles to Concentration Processing of Dilute Pulping Effluents

In this modification of RO for concentration processing and fractionation to achieve pollution control and other routes to effluent treatment, the water contained in relatively dilute process streams is forced under pressure through a membrane in conventional RO modules originally designed for salt water conversion applications. However, the objectives in this program call for a much higher degree of water recovery ranging from 70 percent to more than 95 percent of that contained in the dilute feed waters and also for much higher concentration of the dissolved solids rejected by the membrane system than is normally practiced in salt water and brackish water conversion. Here the degree of pretreatment required, the quality of the concentrate and of the water permeate become matters of added concern, since these products are to be subject to reuse or final disposal without pollution of the water, land, or air environment.

An RO plant will mainly consist of:

(1) A pump for raising the pressure to the chosen operating pressure.
(2) The reverse osmosis membrane unit, in which the feed liquor is separated into water permeate and concentrated liquor.
(3) The recycling pumps for overcoming the frictional pressure drop and for maintaining adequate velocities across the membrane surface.

The minimum energy can be calculated thermodynamically[2]; it is simply the product of the osmotic pressure and volume of the solution. In actual use all processes, including reverse osmosis, use much more energy than this. There are several reasons for the extra energy needed in reverse osmosis. In the first place, although any pressure exceeding the osmotic pressure will cause reverse osmotic flow, achieving a practical rate of flow may require a much higher pressure, perhaps several times as high as the osmotic pressure. Second, as the product water is removed from the dilute pulping liquor feed, the concentration, and therefore the osmotic pressure of the remaining liquor is increased. Finally, there is a significant increase in the membrane fouling as well as frictional pressure drop with increase in the concentration of the liquor.

Complicating the above considerations is the relation of plant cost to operating pressure. A high pressure will increase the product water rate and so decrease the membrane area. This will tend to reduce the cost of the reverse osmosis unit. Against this saving will be the increased cost of energy and pumping equipment.

Another important factor to be considered in the RO plant design is the concentration polarization and fouling of the membrane surfaces. The build-up of fouling materials near the membrane surfaces must be removed by diffusion back into the bulk of the solution; this can be done much more effectively if diffusion is aided by turbulent flow. It has been found experimentally that higher degrees of turbulence and mixing is advantageous in minimizing the concentration polarization and fouling of reverse osmosis membranes.

These general principles will be frequently referred to in subsequent chapters describing the adaptive research program covered in this report.

SECTION V

LABORATORY STUDIES ON THE REVERSE OSMOSIS CONCENTRATION OF EFFLUENTS FROM THE PULP AND PAPER INDUSTRIES

This section deals with the early evaluation studies conducted in the laboratory as a necessary step preliminary to selecting equipment best suited for laboratory, pilot, and field studies. Subsequent laboratory programs were required to develop answers to problems arising in the larger scale work in pilot and field studies. Equipment of various types available from the several suppliers active in the field had to be evaluated in terms of specific process variables, and especially with capability for handling industrial waste flows containing suspended material, colloidal suspensoids, and large molecular weight organics which could foul the membrane assemblies.

INITIAL LABORATORY STUDIES

Equipment

Test Stands — Pumps and Controls

The early exploratory studies on reverse osmosis processing for concentration and fractionation of dilute effluents from the pulping industry, were conducted with a small desk model of a laboratory unit supplied by Gulf General Atomic and designated as their Mark II lab unit. This equipment was designed by the manufacturer to test spiral wound ROGA membrane modules, but in this project, was later adapted to testing other types of small membrane assemblies. This unit had certain limitations, and particularly with the limited rate of flow from its small pump, but it was used effectively and is still in service as problems arise within its capabilities.

For testing larger reverse osmosis membrane modules, a number of Hypro rotary piston pumps were acquired for test stands delivering from 2.5 to 20 gallons per minute at pressures to 600 psig. These units were effective, but were expensive to maintain, since they were not designed for continuous, round-the-clock service required for module life studies. Poor lubricating characteristics of the pulping effluents under test tended to accelerate wear and scoring of the pistons and the need for frequent and costly replacement.

These rotary pumps were in turn replaced with more reliable equipment for sustained operations undertaken within this research and demonstration grant project. Variable stroke reciprocating piston pumps (Model C, Milton Roy, Types MR-1 Simplex and MR-2 Duplex) were mounted on heavy frames with four rubber-tired wheels for ready portability from one site to another. Each portable test stand included one-gallon accumulators for each individual pump, together with supporting pressure gages, back pressure regulator valves (Victor Acme K-20), and instrumented controls and relays for shutting the entire unit down if the desired ranges of liquid level, pressure and temperature were exceeded. These units were also equipped with timers and mechanized valves designed to pulse the unit by bypassing the back pressure control valve to reduce the pressure to zero for brief intervals to achieve normal osmotic flow back through the membrane in handling fouling problems.

A good deal of exploratory laboratory and small pilot study was accomplished with one Simplex pump unit and one Duplex pump unit acquired for preliminary studies conducted prior to undertaking the work under the Federal Research and Demonstration Grant 12040 EEL covered in this report. After starting the grant studies, two additional field test stands of this type, one Simplex and one Duplex, were constructed to extend the program for preliminary field evaluation of various wastes at individual mills. This gave a total of six pumping units on four test stands, all of which have been in continuous service for some four years in and out of our laboratories. One of these units in field service is shown in Figs. 2a and 2b. Individual flow sheets incorporating these units in various demonstration studies are provided in Section VII.

Modular Membrane Equipment

The selection of membrane equipment suitable for pulp and paper effluents was a critical item throughout these studies. The various processing parameters affecting the rate of solvent (water) permeation or "flux" through the membrane were especially critical to the success of this project and were dependent upon maintaining clean hydraulic flows across the surface of the membrane to avoid fouling of the membrane surface. Not all types of equipment on the market could meet the requirements for being able to handle small amounts of suspended solids, and especially of fiber contained in most mill effluents. Again, the membrane system design had to be capable of maintaining sufficient turbulence or velocity across the surface to avoid deposition of precipitates and crystalline material which might be thrown down or which might form slimes or scale during the course of concentrating a mill waste flow. Problems were also apparent in maintaining the membrane equipment free from fouling caused by pitch and other resinous and gummy materials released from colloidal solutions during the course of processing. A breakdown of colloidal suspensoids of pitch and resin particulate matter apparently takes place with changes in pH, temperature, and pressure. The data seemed to indicate that much less fouling was experienced when the breaking of the colloidal sols could be avoided or reduced.

These problems were factors in the selection of equipment to be used from the various types which were submitted for testing. Capillary fiber RO membrane equipment has been shown to have interesting capabilities in the field of processing clear brackish waters, but in these studies could only be used for limited purposes on pulp and paper

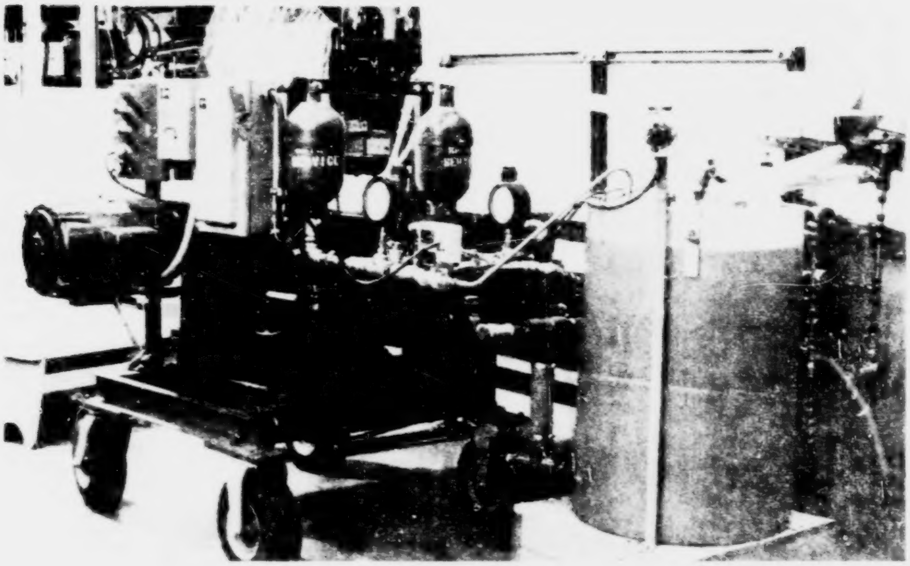


Figure 2a. Milton Roy Duplex Pump on Wheel Mounted Pilot-Scale Test Stand, Complete with Motor, 2 Accumulators, Automated On-Off Controls for Temperature and Liquid Level, and Motorized Valve for Pulsing on Programmed Time Schedule

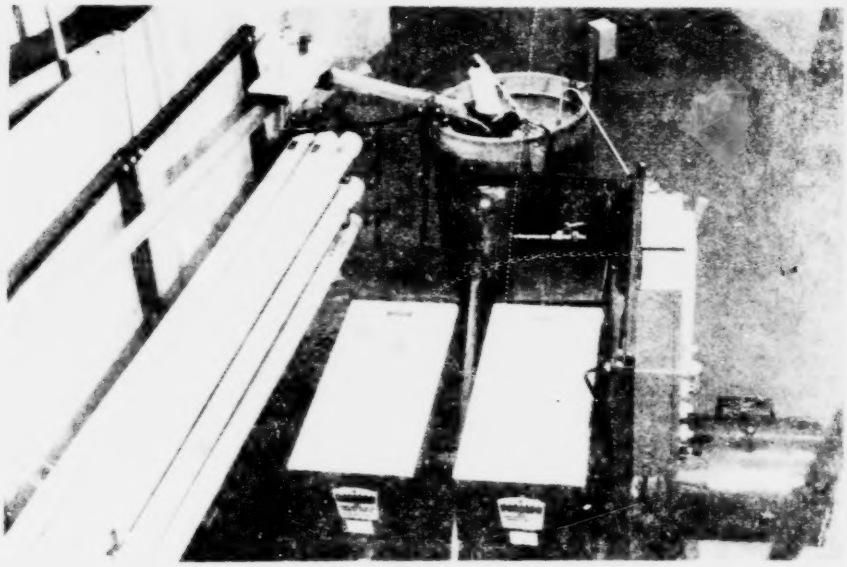


Figure 2b. Photograph of Pilot RO Unit Complete with Instrumented Pump Test Stand, Bank of Modules, and Feed Tank Set up for Continuous Operation on Recycle for Life Tests

wastes, such as the processing of clear evaporator condensates having no carry-over of colloidal material or of suspended matter which could plug the fiber bundles.

Restrictions to free flow were also apparent in the membrane separation structures of sheet membrane pack systems, such as the spiral wound modules which were available for testing in this grant study. Such restrictions made the sheet membrane systems susceptible to plugging with suspended matter much as with the capillary fiber system, though to a lesser extent. However, several promising applications for the sheet membrane (spiral wound) module assembly became apparent during these grant studies, and the suppliers have been modifying these membrane pack assemblies to reduce this problem. The greater ratio of membrane surface area to modular volume should substantially reduce capital and replacement costs, and it is likely that such sheet membrane assemblies may prove economically advantageous in the processing of clear effluents, and for early stages of concentration of very dilute flows up to the point where precipitates and crystalline material may arise as concentration proceeds.

As the picture developed in the preliminary studies and advanced with pilot and field research, it became more and more apparent that of the membrane systems available at that stage of development, tubular systems were best adapted to the overall requirements and objectives for this project. The 1/2-inch tubular systems of Calgon-Havens (Havens International), Aqua-Chem, Westinghouse, American Standard, and Envirogenics (Aerojet-General), have been tested and found to have capabilities for handling the plugging and fouling problems attendant to processing of pulp and paper industry wastes. Tubular systems utilized in this project all had 1/2-inch diameter tubes fabricated with various metal, fiberglass, and resinous materials for the membrane support structures. Cellulose acetate membranes and various formulations are cast in place or inserted into these tubular supports.

Types and Grades of Membranes

Selection of the membranes most effective for these studies was also a critically important problem. Each of the suppliers provided various cellulose acetate formulations and membranes were cast and tempered in various grades of permeability. These grades of permeability tend to be available from different suppliers in from 3 to 5 degrees of "openness." The system of classifying the membranes was not uniform between the various manufacturers, but in general, a No. 1 or No. 2 membrane was most open, and membranes with the highest numerical designation had the greatest degree of tightness and of solids rejection. For control purposes these membranes are usually graded in terms of rejection of NaCl from standard solutions with one gram or five grams of salt per liter. For the purpose of evaluating membrane equipment for processing of pulp and paper mill effluents, these studies tended toward a 3-step standardized system of control tests; first with control tests for flux rate and rejection using city tap water (or distilled water in closely controlled laboratory studies), then with 0.5 percent NaCl solution, and finally with performance tests on a 1 percent "standard" solution of Ca-base spent sulfite liquor solids having various inorganic and organic components in small and large molecular weight classifications. This "lignin liquor" product is available on the market throughout the U.S. as a spent sulfite liquor (SSL) concentrate with 50 percent solids and also as spray dry solids. A 1 percent solution of Ca-base SSL solids has the advantage of providing a solution of colloidal lignin, of various wood-derived sugars and of other characteristic pulping process organics along with inorganic pulping chemicals. A minor disadvantage in preparation and use of the "standard pulping test liquor" arises in that some volatiles as acetic acid and methanol present in the original digester liquors in amounts usually less than 1 percent of the total solids are lost in evaporation and spray drying. These constituents are usually of little significance for the type of tests reported, but they can be added or their absence allowed for if close control of BOD_5 or similar problems are being studied. Tests with the 1 percent Ca-base SSL "standard test solution" will often be referred to in the text and tables of this report.

METHODS AND EXPERIMENTAL PROCEDURES

Samples for laboratory studies were brought in from the mills in quantities suitable for the individual study under way. Routine screening of modules and membranes was usually carried out with use of the 1 percent Ca-base SSL test solution made up from the 50 percent concentrate or of spray dried material from the same source which were available through the courtesy of the Appleton Division of Consolidated Papers. Similar spent liquor products commercially available from other sources around the country have generally proven to be equally suitable for this purpose.

The development of test data on a wide variety of other mill effluents from pulping, bleaching, and papermaking generally involve samples of one gallon to 50 gallons for laboratory study, and even larger quantities were required for sustained module and membrane life studies.

Samples for membrane testing were clarified if necessary through 100-mesh screening prior to use in tubular assemblies. More complete clarification with 3 to 50 µm filtration was practiced for capillary fiber and spiral wound membrane pack processing equipment.

Provision was made for adjustment of pH and the control of temperature as needed for these laboratory test programs. More elaborate pretreatment was seldom resorted to for routine testing, although there were a few instances where various chemical methods of precipitation and flocculation and physical methods of centrifuging, ultrafiltration, and the like, were tried as possible answers to difficult problems. In general, the programs were carried out with little more than screening in the belief that effective membrane processing should be capable of handling industrial waste flows with a minimum of costly pretreatment.

ANALYTICAL METHODS FOR EVALUATION OF PROCESS AND EQUIPMENT

Methods and Experimental Procedures

Various analytical procedures were used to evaluate the performance of the reverse osmosis concentration and fractionation systems on pulp mill effluents. Complete evaluation involved the analysis of the feed liquor to the RO process; of the permeate (product water); and of the rejected solutes in the concentrate stream. Routine assays included total dissolved solids (24 hours at 103-105°C); neutralized 72-hour solids in cases where acid volatiles were present; chemical oxygen demand (COD), NaCl (as chloride); lignin (optical density at 281 nm); 5-day biochemical oxygen demand (BOD_5); pH and color (Co-Pt units). Other specialized assays were used at times.

CRITERIA FOR SELECTION OF MEMBRANE PROCESS EQUIPMENT — EXPERIMENTAL DEVELOPMENT

A first consideration in selecting RO equipment for these studies was based upon performance capabilities of a membrane system for concentrating the solutes in dilute pulp and paper effluents at feed concentrations on the order of 1 percent total dissolved solids (TDS) by a factor of 10 times or more to achieve intermediate concentrates at about 10 percent solids suitable for economic final concentration or disposal by conventional evaporation and combustion systems.

Selection of Membrane Types and Grades (Degree of Rejection or Membrane "Tightness")

The rate of solvent (water) permeation (flux rate) and the impermeability to solutes (the rejection ratios) are dependent upon the "tightness" or "openness" of the membrane at any given pressure level. A variety of different membranes from manufacturers or from research centers were evaluated in our early laboratory studies of reverse osmosis.

A series of experimental runs with controlled tests for comparison of performance of various types and grades of membranes was undertaken. Table 1 summarizes the data derived from membranes in spiral wound "ROGA" modules from Gulf General Atomic (now Gulf Environmental Systems) in three levels of rejection (tight, intermediate, and open membranes) utilizing a first-stage chlorination effluent from bleaching Ca-base acid sulfite pulp.

Flux rates progressed from 6.1 gfd for the tight membrane to 10.9 gfd for the open membrane, and the corresponding rejections were on the order of 50 percent or less for the open membranes and 90 percent or more for the tight membrane. For the purpose of reusing the clear water recovered at the 80 percent level in the permeate, the intermediate membrane grade apparently performed with the best economy to give satisfactory quality of water for reuse.

TABLE 1

EFFECT OF MEMBRANE "TIGHTNESS" ON PRODUCT WATER QUALITY

Chlorination stage sulfite bleach effluent
Spiral wound modules
450 psig - 25°C
1.8 gpm - Feed rate
80 Percent water recovery

Sample	Flux, gfd	Solids, mg/l[a]	COD, mg/l[a]	Chloride, mg/l[a]	pH	Optical Density at 281 nm[b]
Process feed		1960	945	430	2.2	8.75
Product water						
Tight	6.1	14	100	36	2.6	0.194
Intermediate	7.0	72	132	251	2.2	0.261
Open	10.9	822	516	400	2.3	3.63
Concentrate						
Tight		12120	6655	3260	2.2	80.4
Intermediate		6440	4366	1964	1.9	44.8
Open		5160	3405	852	2.2	31.7

---

[a] Based on composited samples for each recovery level.
[b] A measure of the lignin content.

A second and similar test of tubular membrane equipment using higher grades of membrane tightness available from Havens Industries (Type 3 — intermediate; Type 4 — moderately tight; and Type 5 — tight) confirmed this picture and extended the data at various levels of 32, 60, and 85 percent water recovery (Table 2).

A third test (Table 3) in this series compared the open Type 2A Havens membrane with the intermediate Type 3 membrane at 40, 60, and 90 percent water recovery. The flux rates for the open membrane remained high, but the solids and chloride rejections were reduced below the 50 percent level as the water recovery advanced to the 60 and 90 percent levels.

These data have been confirmed repeatedly in an extensive continuing evaluation on other waste flows, and were the base for establishing equipment specifications for this project at the intermediate degree of membrane tightness to achieve economic feasibility in terms of

TABLE 2

CONCENTRATION WITH TUBULAR UNITS WITH THREE DIFFERENT MEMBRANE "DEGREES OF TIGHTNESS"

Ca-Base acid sulfite first stage bleach effluent
650 psig Operating pressure
Temperature 25°C
4 gpm Feed rate - recycle flow

Havens Membrane	Flux, gfd	Solids, mg/l	COD, mg/l	Chloride, mg/l	Optical Density at 281 nm[a]
Process feed		1586	988	370	7.4
		For 32 Percent Water Recovery			
Product water					
Type 3	14.7	21	104	63	0.090
Type 4	8.7	16	84	16	0.063
Type 5	8.1	13	88	19	0.051
Concentrate		1804	1174	551	9.4
		For 60 Percent Water Recovery			
Product water					
Type 3	13.5	64	102	83	0.102
Type 4	10.2	48	76	17	0.065
Type 5	9.0	31	78	13	0.066
Concentrate		3124	1687	850	14.7
		For 85 Percent Water Recovery			
Product water					
Type 3	8.3	368	144	198	0.211
Concentrate		9239	5070	2131	45.9

---

[a] A measure of the lignin content.

TABLE 3

CONCENTRATION WITH TUBULAR UNITS CONTAINING TYPE 2A (OPEN) AND TYPE 3 (INTERMEDIATE) MEMBRANES

Ca-base acid sulfite first-stage bleach effluent
650 psig Operating pressure
25°C Temperature
4 gpm Feed rate - recycle flow

Sample	Water Recovery, percent	Flux gfd	Solids, mg/l	COD, mg/l	Chloride, mg/l	pH	Optical Density at 281 nm[a]
			For Type 2A Open Membrane				
Process feed			1344	655	411	2.3	7.0
Product water							
1	40	20.9	602	147	313	2.8	0.88
2	60	30.7	816	162	370	2.7	1.04
3	90	22.6	1038	244	466	2.5	1.68
Concentrate			6928	5655	741	2.3	30.4
			For Type 3A Intermediate Density Membrane				
Process feed			2200	1200	540	2.4	12.0
Product water							
1	90	8.0	22	54	15	2.3	0.067
Concentrate			53300	25100	12490	2.4	250.0

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[a] A measure of the lignin content.

practical rates of flux and of recovery of dissolved components in the concentrate and relatively clean reusable permeate waters. Almost all studies thereafter were conducted with membranes of intermediate levels of tightness equivalent to Havens Type 3. Occasional trials were made from time to time with new membranes coming from a continuing program of research and development conducted at universities and by individual suppliers. Late in 1970 reports became current of substantial improvements becoming available in the flux rates for tighter membranes from several suppliers, and such membranes in single test modules did become available for preliminary testing in the Spring months of 1971, as reported in Section IX, but this project was at that time in the final phases of completion, and a significant program of testing could not be undertaken for review in this report.

MODULE DESIGNS

The first modular equipment available for laboratory studies was of the spiral wound design. This system had a number of engineering design and economic advantages for processing large quantities of dilute effluents, namely:

a. The large area of membrane per unit of equipment volume would result in reduced overall space requirements, compared to other styles of module arrangement, tubular or plate-frame.

b. The diameter (and area) of the modules could be adjusted during manufacture to fit any size pipe.

c. The modules could be readily placed in series or parallel operation.

d. The use of sheet membranes and larger membrane surface to module volume ratio has significant cost advantages both for capital cost and also the important operating charge category of membrane maintenance and replacement.

The flow pattern through thin separator channels between membranes was, however, more subject to plugging by feed liquors containing particulate matter, or from which precipitates formed during concentration. In the processing of mixed first and second stage bleach effluents (kraft or sulfite), for example, precipitates slowly formed and settled within the module flow paths and on the surfaces of the membrane even after filtration through a 50 µm filter. Periodic backwashing cycles to remove the precipitated, crystalline scale, partly alleviated the problem, but this procedure would add markedly to the cost of commercial scale operations.

The clear hydraulic flow pattern of tubular-type modules has been found more adaptable to the processing of pulping effluents containing particulate matter (fibers) and constituents with low solubility products (calcium sulfate and calcium sulfite) which have caused module plugging in the more restricted flow channels of other module designs.

First and second stage kraft bleach effluents and mixtures of the two could be processed without clarification for the production of high quality water and a four- to fivefold concentration of the solids (Table 4).

Tubular modules from five manufacturers have been evaluated in our laboratories along with two spiral wound designs and a hollow fiber system. The excellent area/volume ratios previously referred to for the spiral wound modules are markedly extended in the hollow fiber concept. A pressure vessel 0.5 inch in diameter and five feet long can accommodate 18 square feet of membrane surface. At the same time, the plugging characteristics of the thin-flow patterns have been intensified by the natural filtering capacity of the fiber bundles. In this experience, feed streams containing particulate matter required

TABLE 4

PROCESSING CLARIFIED AND UNCLARIFIED KRAFT BLEACH PLANT EFFLUENTS THROUGH TUBULAR MODULES

Type 3A Membrane
450 psig Operating pressure
Temperature 25°C
2 gpm Feed rate - recycle flow

Sample	Water Recovery, percent	Flux, gfd	Solids, mg/1	BOD, mg/1	COD, mg/1	Chloride, mg/1	Optical Density at 281 nm[a]
Clarified Chlorination Stage			3120	570	2050	1140	9.7
Product water							
1	20	5.7	90	--	200	40	0.157
2	40	6.3	86	--	262	35	0.167
3	60	6.7	100	--	242	72	0.146
4	80	6.5	131	166	269	60	0.167
Concentrate			--	800	8625	5025	23.0
Unclarified Chlorination Stage			3345	590	2130	975	9.7
Product water							
1	20	5.27	52	--	222	20	0.072
2	40	6.0	50	--	228	28	0.058
3	60	6.5	57	--	228	23	0.067
4	80	6.5	75	62	231	35	0.074
Concentrate			15475	1000	8700	4900	--
Clarified Alkaline Wash			1335	--	550	335	0.15
Product water							
1	20	5.5	25	--	18	12	0.036
2	40	5.8	24	--	18	12	0.029
3	60	6.8	24	--	17	9	0.033
4	80	7.1	30	--	19	16	0.039
Concentrate			5350	--	1608	1412	--
Unclarified Alkaline Wash			1230	60	550	320	0.19
Product water							
1	20	4.7	48	--	25	12	0.034
2	40	5.7	32	--	22	20	0.027
3	60	6.2	23	--	17	8	0.024
4	80	6.5	32	14	12	21	0.028
Concentrate			4300	625	1076	1368	0.79

---

[a] A measure of the lignin content

careful filtering (5 µm or less) prior to processing in the capillary fiber system.

In some cases, such as with evaporator condensates, the feed streams are relatively free of suspended materials and low solubility constituents. Capillary fiber systems were tried with evaporator condensates and tended to confirm these expectations, but still with practical problems apparently arising from uncontrolled microbiological growth and the tests were terminated.

PULP AND PAPER PROCESS EFFLUENTS TESTED

Acid Sulfite Pulping

Ca-Base Standard Test Liquor

Ca-base "lignin liquor" has been adopted for the purpose of this project to fill the need for a standard liquor upon which comparative control tests could be established throughout the entire program of 3-1/2 years of research and field studies. Calcium-base acid sulfite digester liquors at 10 to 14 percent solids are evaporated to 50 percent solids concentration and the resultant "lignin liquor" is marketed commercially in that form nationwide, and also as a spray dry product. This product was usually diluted with tap water to 1 percent concentration as a standard for the frequent control tests.

Ca-Base Acid Sulfite Pulp Wash Water

This product is available from advanced stages of washing or "cooling" of the pulp and was tested as received at about 1 percent solids ± 0.5 percent.

Acid Sulfite Evaporator Condensate

Many acid sulfite mills evaporate their strong liquors. Volatile acids as; SO_2, acetic and formic acids, and other volatiles are contained in the evaporator condensates and comprise a major source of BOD in the total effluent flow from an acid sulfite pulp mill.

Acid Sulfite Bleach Plant Effluents

Two such effluents, one a first stage chlorination effluent and one a single-stage Ca hypochlorite effluent were tested.

NH_3-Base Acid Sulfite Wash Waters

Similar to wash waters from Ca-base acid sulfite wash waters.

Mg and Na-Base High-Yield Bisulfite Wash Waters

Similar to Ca and NH_3 base, but usually have higher pH levels due to the cooks with high levels of bisulfite to achieve higher pulp yields.

Neutral Sulfite Semichemical "White Water"

The pulp wash water from on-machine washing of paperboard pulp and related products is referred to as "NSSC white water" in common with the terminology for the fiber containing effluent draining from paper machines.

Kraft (Alkaline Sulfate) Pulping

Kraft Pulp Wash or Rewash Waters

These effluents may exist as residues in older kraft mills, but in most cases are being systematically eliminated as mills are modernized or replaced with new continuous digesters having in-digester washing. Nearly all residual waters are recycled and pass on to the evaporators and chemical recovery systems. These flows no longer appear to be a large problem needing study by the RO route. Study of a rewash water was initiated early in this project but the work was terminated short of a full-scale field demonstration.

Kraft Bleach Effluents (KBE)

The bleach plant effluents of kraft pulping comprise a major source of the remaining incompletely solved water pollution problems in the kraft pulping branch of the industry. High levels of dilution are characteristic (10,000 to 30,000 gal./ton bleached pulp), and although BOD_5 loads are relatively low (30-50 lb/ton pulp production), the color, the content of resistant organics with high COD, and the substantial level of inorganic salts (NaCl, Na_2SO_4) are of concern. Usually there exists a multiplicity of effluents from the various bleaching operations or sequences such as in (CEDED), in which the first stage of chlorination (C) (low pH) is followed by two stages of alkaline extraction (E) alternating with two stages of low pH chlorine dioxide (D) bleaching. Tests conducted within this RO research and field demonstration grant project included substantial trials and a field test on second-stage caustic extraction effluent and with lesser studies on the first stage chlorine (C) effluent.

Kraft Evaporator Condensates

These condensates can be substantial air and water pollution problems from kraft recovery systems, but preliminary testing was not promising and these wastes were not included in the program here reported.

Barking Waters

The barking of wood is usually conducted with late-stage recycle waters which derive from various mill sources low in BOD_5 and chiefly comprise problems of dealing with suspended solids and fines in primary clarification systems. Preliminary tests for evaluation of possibilities for concentration of low levels of solubles were conducted in this study, but the importance and feasibility of such processing remained in question, and large-scale tests were not attempted within the budget limitations of this project and availability of time of the staff.

Paper Mill Effluents

Various small-scale tests on paper machine dye wastes, coating wastes, and machine white waters were conducted, but the limitations of cost for processing such extremely dilute (0.1 percent TDS or less) effluents could not justify RO concentration processing by factors which would range upwards of perhaps 100 times or more. Other methods of disposal processing of such dilute waste flows appear more practical at this stage of developing the membrane processes.

Deinking Wastes

This type of waste high in content of coating clays, hydrocolloids, and printing ink residues is a critical problem for which membrane processing has been considered and tested in a preliminary way. Results have been marginal. Further study may change this picture.

Technically, the testing program has shown that high quality water for recycle and reuse can be recovered from all of these wastes by reverse osmosis under properly controlled conditions of fluid velocity, pH, temperature, and control of changes in state for colloidal materials. Commercial feasibility as a means of concentrating dissolved pollutants is quite another matter, and the prospects of large-scale application are limited to those effluents having a suitable range of concentration of dissolved materials and of effluent volumes upon which capital and operating costs can be justified. Pulp wash waters at about 1 percent solids concentration from which chemical values, clean reusable waters for recycle, and major pollutants can all be recovered have been of first concern and have received priority in this study.

Rejection Ratios

The degree to which an RO membrane is capable of rejecting and concentrating solutes from the feed liquor to produce clean reusable permeate waters is a primary consideration in close association with the permeate flux rates. The rejection ratio is calculated by the formula:

$$\text{Percent Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (4)$$

where

C_p = concentration of the constituent in the product water
C_f = concentration of the same material in the original feed

The rejection ratio ranges summarized in Table 5 have been achieved for the pulp wash waters and bleach effluents tested and to lesser extent in such cases as with volatiles, which pass freely through the membranes at low pH levels, as summarized in Table 6. Acid volatiles may be neutralized and concentrated with technical success, but the economics have yet to be developed on this type of waste flow.

TABLE 5

PERCENT REJECTION FOR TYPICAL PULP WASH AND BLEACH EFFLUENTS

600 psig Operating Pressure
Temperature 25°C

Constituent	Membrane Type Intermediate	Tight
Solids, total	75-98	95-99
Optical density (color)	98-99.8	99-99.8
Biological oxygen demand (BOD)	80-95	90-99
Chemical oxygen demand (COD)	85-98	90-99
Inorganics	60-95	94-99

TABLE 6

PERCENT REJECTION DURING THE RO CONCENTRATION OF CONDENSATES FROM THE EVAPORATION OF SPENT SULFITE LIQUORS

600 psig Operating Pressure
Temperature 25°C

	Intermediate Membrane			Tight Membrane		
Constituents	pH 2.7	pH 4.8	pH 6.1	pH 2.7	pH 4.8	pH 6.1
Solids, total	27	57	70	45	81	95
Optical density (color)	66	55	48	79	74	90
Biological oxygen demand	26	45	58	52	62	82
Chemical oxygen demand	39	43	57	37	62	81
Volatile acids (as acetic)	7	40	65	26	70	95

Process Variables

Temperature

Processing temperature was from the first considered to be an important parameter of operation. Prior experience had indicated an increase in temperature from 10 to 31°C would approximately double the permeation rate for a given membrane at a single pressure level[1,5]. Later studies[6] with a calcium-base acid sulfite liquor in the concentration range of 12 to 104 grams solids per liter (osmotic pressure 125-200 psi) confirmed the temperature effect to be on the order of 2.1 percent per degree centigrade at the 12 g/l concentration and was not significantly different at the 104 g/l level. A search for membranes capable of operating at 40°C or above continued throughout the project not only to achieve advantage from higher flux rates but also to reduce requirements for expensive cooling pretreatment for warm or hot feed liquors.

Fluid Velocity

Concentration polarization, the formation of stagnant layers of fluid at the membrane surface, produces several effects detrimental to the efficiency and economics of membrane separation processes:

1. The osmotic pressure of the stagnant layer increases with rising solute concentration and the effective pressure for the permeation of solvent through the membrane decreases, thereby increasing the pumping power requirements.
2. Concentration polarization decreases the quality of the permeating solvent (water), since the increase in the solute concentration at the membrane surface increases the transport of solute through the membrane.
3. The decrease in permeate quality may adversely affect the membrane and cause accelerated deterioration; concentration polarization could aggravate this effect.
4. Concentration polarization may result in precipitation of marginally soluble solutes, thereby causing scaling on the membrane surface and resulting in a loss of solvent permeation.

The first technical papers describing results of this project[1,5] presented data experimentally derived on the linear velocity required to process various effluents in one-half inch inside diameter tubular modules. Velocities necessary to minimize concentration polarization were on the order of 35 cm/sec at 7 grams solids per liter, 60 cm/sec at 36 g/l, and 80 cm/sec at 95 g/l; or in all cases Reynolds numbers in excess of 5000.

A third paper[6] related the viscosity of the various process streams to Reynolds numbers for various solids levels and temperatures indicated that turbulent flow was considered to occur at Reynolds numbers above 4000. A velocity of approximately one foot per second (30 cm/sec) should be sufficient to produce turbulent flow in the temperature range of 25-35°C for solids concentrations of about:

2 percent or less for neutral sulfite semichemical white water.

3 percent or less for ammonia-base acid sulfite and second-stage kraft bleach effluents.

4 percent or less for calcium-base acid sulfite liquors or wash waters in 0.5 inch ID tubular modules.

For higher concentrations, a velocity of one foot per second may or may not be in the turbulent range, depending upon the temperature and viscosity of the process feed.

pH

A marked decline in flux with increasing feed pH was observed in early laboratory trials. As a general rule, a change in the pH away from the normal level of pH for the waste stream resulted in a decrease in the transport of water through the membrane. This did not appear to be due to membrane changes *per se*, as there was no significant difference in the flux rate with a water feed between the pH of 3 and 8.

The pH change necessary to avoid hydrolysis of cellulose acetate membranes increased the possibility of the formation of insoluble materials in some feed streams. In these cases the adjustment of the pH in effluents containing suspensoids in the colloidal, semiflocculating, or other dispersed states apparently resulted in coating of the membranes and a loss in flux rate.

Little, if any, effect upon rejection ratios was apparent in changing the pH for most of the wastes under investigation, but the effects were substantial and quite important in the case of evaporator condensates. Neutralization of low molecular weight volatile acids as acetic acid converted these to larger molecular weight salts that were well rejected.

Pressure

Although the equation:

$$F_w = aE\ (\Delta p - \pi) \qquad (5)$$

where

F_w = rate of water permeation, in gfd
a = membrane area, sq ft

E = membrane constant
Δp = pressure differential across membrane, psi
π = osmotic pressure of process steam minus product water, psi

generally holds for the overall processing of the pulping waste streams, there are other pressure related factors which must be taken into account, such as membrane compaction which may produce changes in the rejection ratio, as well as in flux rate.

The effect of pressure on the flux rates, while processing bleach effluents, was the subject for study early in this project and was found to deviate from the usual directly proportional relationship. In the case of studies with the spiral wound modules (Table 7) data indicated a deviation from linearity which approached a 2:1.5 relationship between pressure and flux.

Some of this deviation was traced to membrane compaction while processing distilled water with old and new tubular modules (Fig. 3). In later, carefully controlled studies with a large number of 18-tube modules, this was shown to be due to an almost linear decrease in the Membrane Constant (E) with increases in the applied pressure.

While it would appear from the data in Table 7 that there was an increase in the rejection ratios with increased pressures, this has not been borne out in large-scale operations to date. After the initial compaction of the membrane, there appears to be an increase in the membrane rejection roughly proportional to pressure increases for some of the effluent constituents (chlorides). However, this relationship does not extend to all components, such as color bodies in the waste stream.

Process Modification Studies for Operating Problems Encountered in Field Studies

After most of the process variables had been identified, their effects determined, and all possible means for their control had been developed to maintain the process under adequate control for obtaining good research data, search began for process modifications which would permit sustained operation for the reverse osmosis concentration of the broad range of pulping effluents. In some laboratory and field trials unexpected problems were encountered which raised questions as to the usefulness of RO for the concentration of certain of these process effluents.

The laboratory studies have since developed answers to most of these problems and with suitable modifications in pretreatment or in operating procedures, it appears that almost all pulp and paper waste streams studied can be successfully concentrated on a sustained continuous basis.

TABLE 7

RO PROCESSING AT DIFFERENT PRESSURE LEVELS WITH SPIRAL WOUND MODULES

Kraft Second-Stage Bleach Effluent
Temperature 25-32°C

Operating Pressure, psig	Flow Rate, ml/min		Chloride Concentration, mg/l		
	Concentrate	Product Water	Feed	Concentrate	Product Water
		First Trial			
100	370	10.2	310	310	--
250	338	33.0		330	90
400	305	51.0		400	80
		Second Trial[a]			
100	397	12.8	339	350	10
250	375	30.5		360	9
400	348	46.4		370	8

[a] Second trial started 24 hours after first trial.

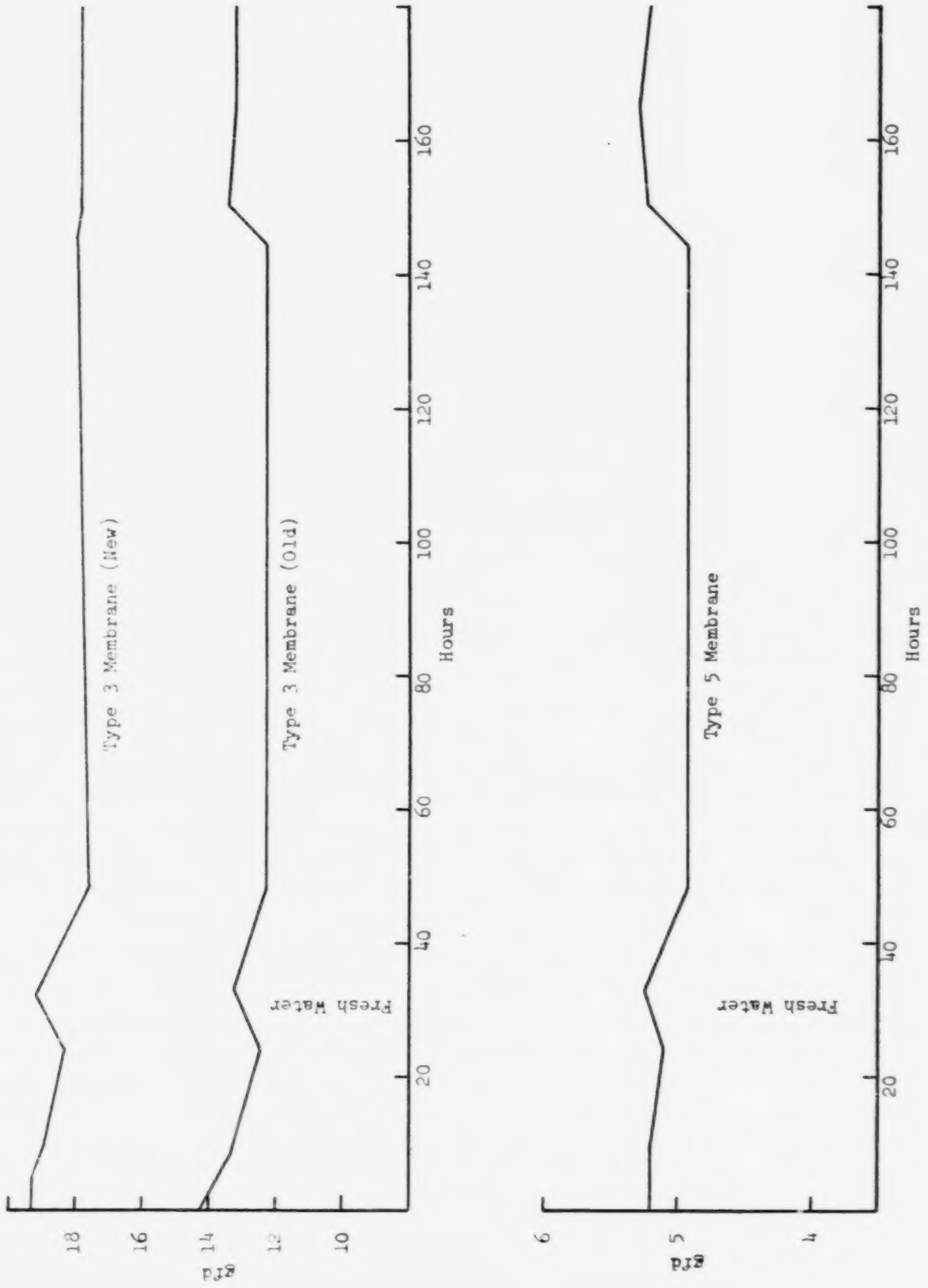


Figure 3. Evidence for Membrane Compaction (Distilled Water at 600 psig and 25°C)

Microbiological Slimes

Many of the pulp and paper process effluents subject for study in this project contain wood sugars and other fermentable carbon compounds derived from the wood and also other nutrients which allow substantial microbiological growth. Slime formation can be a serious problem. Long holding times or recycle at certain temperatures and pH levels promote such growth and membrane process systems must be properly designed to reduce or eliminate this problem.

The RO equipment available for early studies was not designed to that end and experience quickly showed up these deficiencies. The problem was especially apparent in the capillary fiber and spiral wound assemblies when operated on a recycle feed system.

Tubular RO systems capable of being operated with high velocities, to achieve a flushing action across the surface of the membrane, reduced the microbiological sliming problem substantially but even so there was much evidence of unacceptable levels of flux loss due to fouling with microbiological growths. In certain cases, such as with the module life studies, where the process liquors were under continuous recycle conditions for extended periods of time, there were even problems with slime pads blocking the operation of the pressure regulating valve.

A "ball-flushing" procedure proposed by Dr. Loeb of the University of California was first used in the life studies to maintain clean membrane surfaces. This consisted of passing a slightly oversize (3/4-inch) ball of soft polyurethane foam through the 1/2-inch ID tubes of a module at atmospheric pressure.

While this helped to maintain the flux rates at high levels, there were several difficulties:

> The construction of the modules was such that it was difficult to pass the ball through a number of modules in series and this limited the usefulness of the procedure for large installations such as the trailer unit (387 Modules).
>
> It was feared that the presence of hard sharp scaling particles on the surface of the membrane might result in scratching of the active surface of the membrane, resulting in leaks and loss of rejection.
>
> Later trials indicated that a number of procedures could be used to reduce or eliminate the formation of slimes in the process liquor, including:

a. The use of biocides such as alkyldimethylbenzylammonium chloride (Zephiran) was helpful in systems which required recycling.

b. Straight-through operation with low holding time and high velocities permitted slime-free operation of modules which had been thoroughly clean at the start of the process period.

c. Operation of the system at elevated temperatures above (45-55°C) reduced or eliminated microbiological growth problems in all cases where the membrane could withstand such temperatures in sustained operation. Cellulose acetate membranes are not usually recommended for temperatures above 40°C and some manufacturers limit use of their products to 35°C which is ideal for microbiological growth.

d. The use of chlorination or ultraviolet light for the sterilization of the incoming feed stream has been tried with some success to clear, colorless process streams. Ultraviolet light is, however, absorbed in colored pulping effluents and can be expected to have limited use in such cases.

Low BOD Rejection of Low Molecular Weight Fermentable Materials

In the module life studies, which entailed a feed recycling system with fresh liquor makeup every other day, a wide range of BOD_5 rejection values were noted. These rejections were lower than those achieved in single pass operations with the same feed and module system.

The only readily apparent difference between the two systems was the time interval between sampling of the feed and product water streams. In the single pass unit, the interval between the time that the feed was sampled and the composite product water sample was taken was usually not more than three hours. In the recycle system, however, the feed sample was taken immediately after makeup and the product water was sampled the following morning to permit equilibration of the process.

Tests with dyes and tracers indicated that at a 3 gpm flow rate and 600 psig operating pressure with the Type 3 modules, the system could be brought to equilibrium within an hour or less. With this factor under consideration, a series of BOD_5 analyses were set up on sampling periods of 1-1/2 hours, as well as the 24-hour sample. Data in Table 8 indicate a marked difference in the rejection values for the two sampling periods. The a, b, c, etc., samples, which were taken 1-1/2 hours after feed makeup, had BOD_5 rejections in excess of 98

TABLE 8

BOD$_5$ REJECTION ON 18-TUBE MODULE LIFE STUDY-EFFECT OF SAMPLING TIME ON REJECTION VALUE

		BOD$_5$, mg /l		
Sample	Date	First[a] Sample	Second[b] Sample	BOD$_5$ Rejection, percent
Fa	9/6	1785		
Pa	9/6	93		95
Fb	9/9	2018		
Pb	9/9	95		95
Fc	9/11	2110		
Pc	9/11	80		96
Fc'	9/12		2140	
Pc'	9/12		340	84
Fd	9/13	2085		
Pd	9/13	92		96
Ff	9/18	2268		
Pf	9/18	127		94
Ff'	9/19		2168	
Pf'	9/19		300	86
Fg	9/20	2210		
Pg	9/20	111		95
Fh	9/23	2505		
Ph	9/23	109		96
Fi	9/25	2455		
Pi	9/25	180		93
Fi'	9/26		2455	
Pi'	9/26		251	78
Fj	9/27	2275		
Pj	9/27	128		94

F - feed
P - permeate

---

[a] First samples taken 1-1/2 hours after fresh feed make-up.

[b] Second samples taken 24 hours after fresh feed make-up.

percent, while those taken the following day (a', b', c', etc.) were generally below 85 percent. Sugars readily rejected could be degraded to nonrejected volatiles.

Fouling by Organic and Inorganic Coatings, Colloidal Suspensoids, and Crystalline Scale Deposits

Rapidly decreasing flux rates with tubular modules, while processing volumes (50-100 gal.) of certain wastes, indicated some factor other than osmotic pressure or membrane compaction might be responsible for the loss. This was especially apparent when these same effluents could be concentrated in small volumes without marked flux losses as long as the flow paths were not plugged.

Data obtained in processing 50-gal. quantities of second-stage kraft bleach effluent (caustic KBE) using old and new Type 3 and Type 5 modules, are plotted in Fig. 4. The flux decline for the older Types 3 and 5 modules, which had lower initial flux rates, was less than for the new Type 3 membranes, the flux losses of which were significant in the first ten hours and were still declining after 118 hours of operation.

Tubes from these modules at the end of the trial had a coating on the membrane surfaces. These coatings had not appeared, or were not present in observable amounts, when smaller volumes were processed. Therefore, some waste streams under investigation probably contained small quantities of materials (not microbiological slimes) which could coat the membranes over a period of time.

During several trials with acid sulfite pulp wash waters, pitch deposits, as well as calcium sulfate scaling of the membrane surfaces were encountered. Other process streams also contained materials, either in colloidal suspensions or of limited solubilities, which if processed to high concentrations would precipitate and coat the membranes.

Water Washing

In a field trial with a wash water from calcium acid sulfite pulping of sprucewood large quantities of "pitch" deposited on the walls of the feed tank in the foam layer produced by the splashing of the incoming liquor.

After collecting some of this deposit, a laboratory study was made of a water suspension of the pitch with a single tube module. This module was constructed from an old 7-tube module by repositioning the end caps to provide straight-through flow in a single tube. The flow sheet (Fig. 5) details the basic design and modifications of this setup for processing small volumes of material.

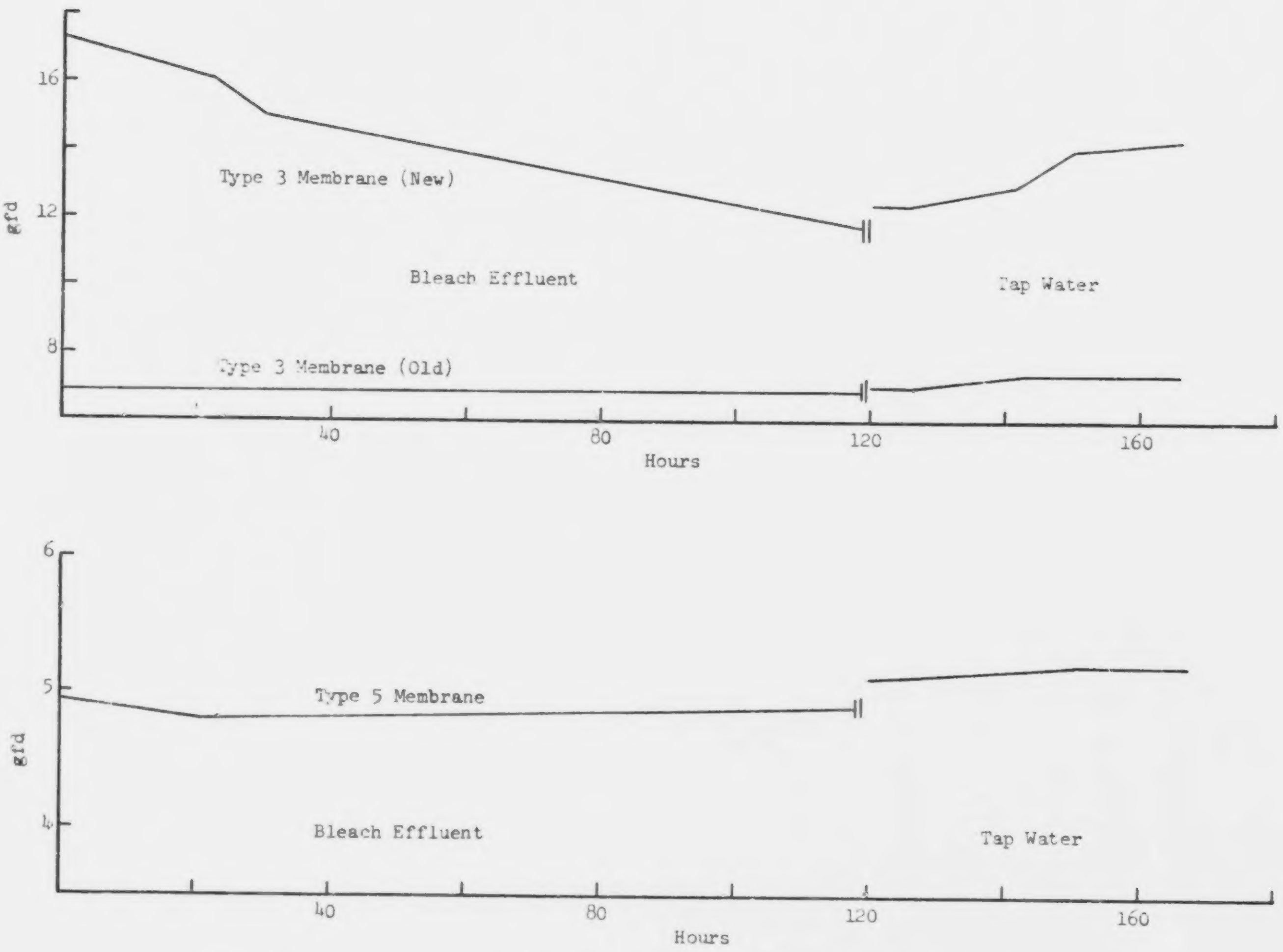
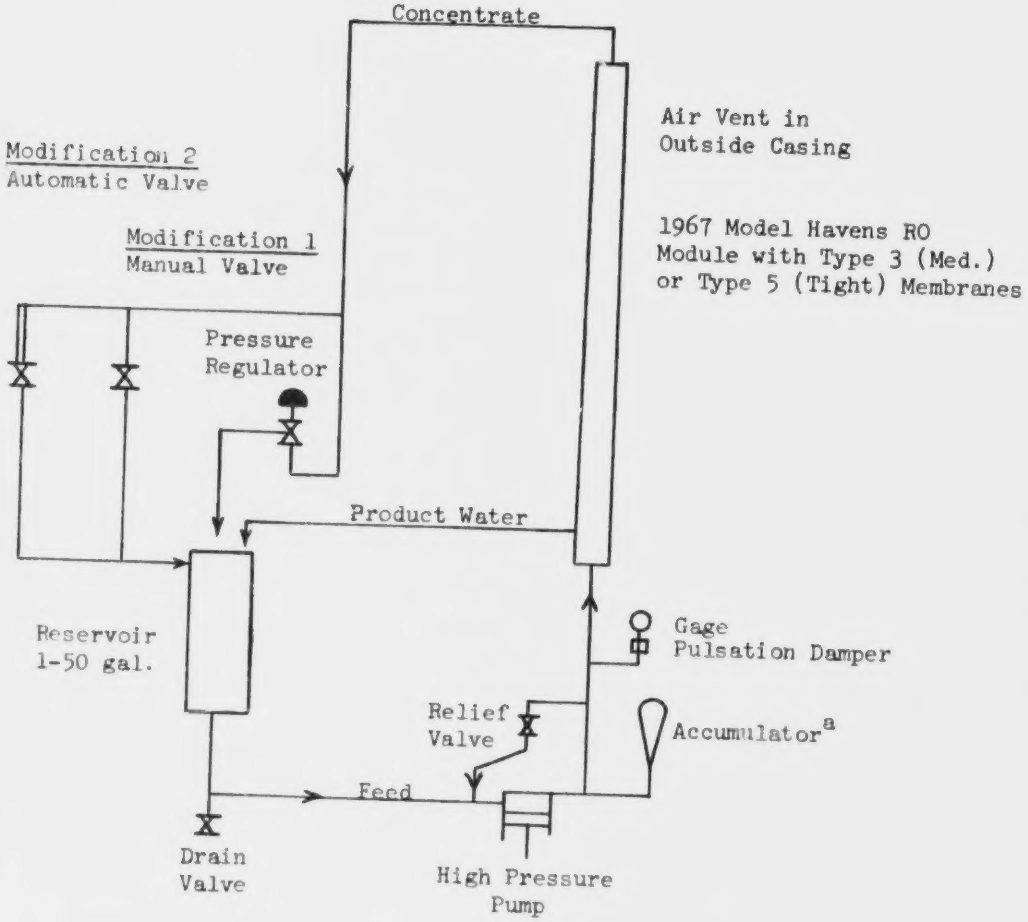


Figure 4. Flux Rates from Coated (Fouled) Membranes (Caustic KBE at 600 psig at 25°C)


Concentrate
Air Vent in
Outside Casing
Modification 2
Automatic Valve
Modification 1
Manual Valve
1967 Model Havens RO
Module with Type 3 (Med.)
or Type 5 (Tight) Membranes
Pressure
Regulator
Product Water
Reservoir
1-50 gal.
Gage
Pulsation Damper
Relief
Valve
Accumulator[a]
Feed
Drain
Valve
High Pressure
Pump

[a] A one quart size Greer Olear bladder type (water service) accumulator.

Figure 5. Equipment Set-up for Reverse Osmosis Processing with a Single Module

The results (Table 9) for the processing of this reconstituted deposit in water, show a progressive decline in the flux rate with time. The flux rate could, however, be partially restored by a brief water washing. Periodic washes or flushing with clear tap water appeared to be one route for control of certain types of membrane fouling and to maintain high flux rates for water transport through the membrane.

TABLE 9

PRODUCT FLUX RATES VS TIME

Reconstituted Pitch From Filters at Consolidated
Single Tube Havens Module - Type 3
500 psig Operating Pressure
Temperature 25-35°C

Time, minutes	Product Water Flux, corrected to 25°C ml/min.	gfd	Percent of Initial
0	27.4	11.1	100
60	22.3	9.1	82
120	22.0	8.9	80
180	23.6	9.5	86
240	23.6	9.5	86
300	23.2	9.4	84
360	23.4	9.4	85
420	23.4	9.4	85
1410	19.5	7.9	71

Pretreatment for Removal of the Fouling Agent

A loss in flux rate was noted while processing NSSC pulp wash water in studies of the optimization of the fluid velocity across a membrane at different concentrations. This was traced to micelles (ray cells) in this waste stream which were deposited on the membrane surfaces whe their colloidal state was destroyed.

Pretreatment studies based on the removal of these materials by the addition of filter aids and filtration were partially successful in reducing, but not completely eliminating, flux losses. The addition of filter aid or carbon to adsorb the fouling agent, without removal by filtration, was completely unsuccessful in removing the "fouling' constituents from a kraft rewash water (Table 10).

TABLE 10

EFFECT OF VARIOUS PRETREATMENTS REVERSE OSMOSIS PROCESSING OF KRAFT PULP WASH WATER

Calgon-Havens Single-Tube Unit at 600 psig

Pretreatment	Flux Rate		
	0-Hour, gfd	22-Hours, gfd	Loss, percent
None	14.9	8.3	46
Aerated and mechanically stirred[a]	15.6	10.4	32
Mechanically stirred only[a]	15.6	10.8	31
Aeration without mechanical stirring[a]	15.8	10.9	31
None but "hard pressure-pulsed" 30 sec./hr.	14.6	14.3	2.0
		13.2 at 46 hr.	9.6
		11.9 at 54 hr.	18

---

[a] Foam skimmed periodically for 1 hour.

Pressure Pulsing

During the trials with both treated and untreated effluent samples, we had observed an increase in the flux rates after short periods of pressure reduction to atmospheric levels (Fig. 6 and 7). Further development of this "pressure pulsing" technique resulted in a process modification which permitted sustained operation, even in the presence of fouling agents. Flux rates were sustained at 85-99 percent of the initial water permeation rate. Experience with pressure pulsing in these studies when concentrating pulp and paper effluents was more favorable and consistent than the experience reported by Kopecek and Sourirajan[7], who favored extended treatment with elevated back pressure to restore flux rates. Apparently, the pressure pulsing applies more to flushing out of foulants while back pressure treatment relieves sustained membrane compaction problems.

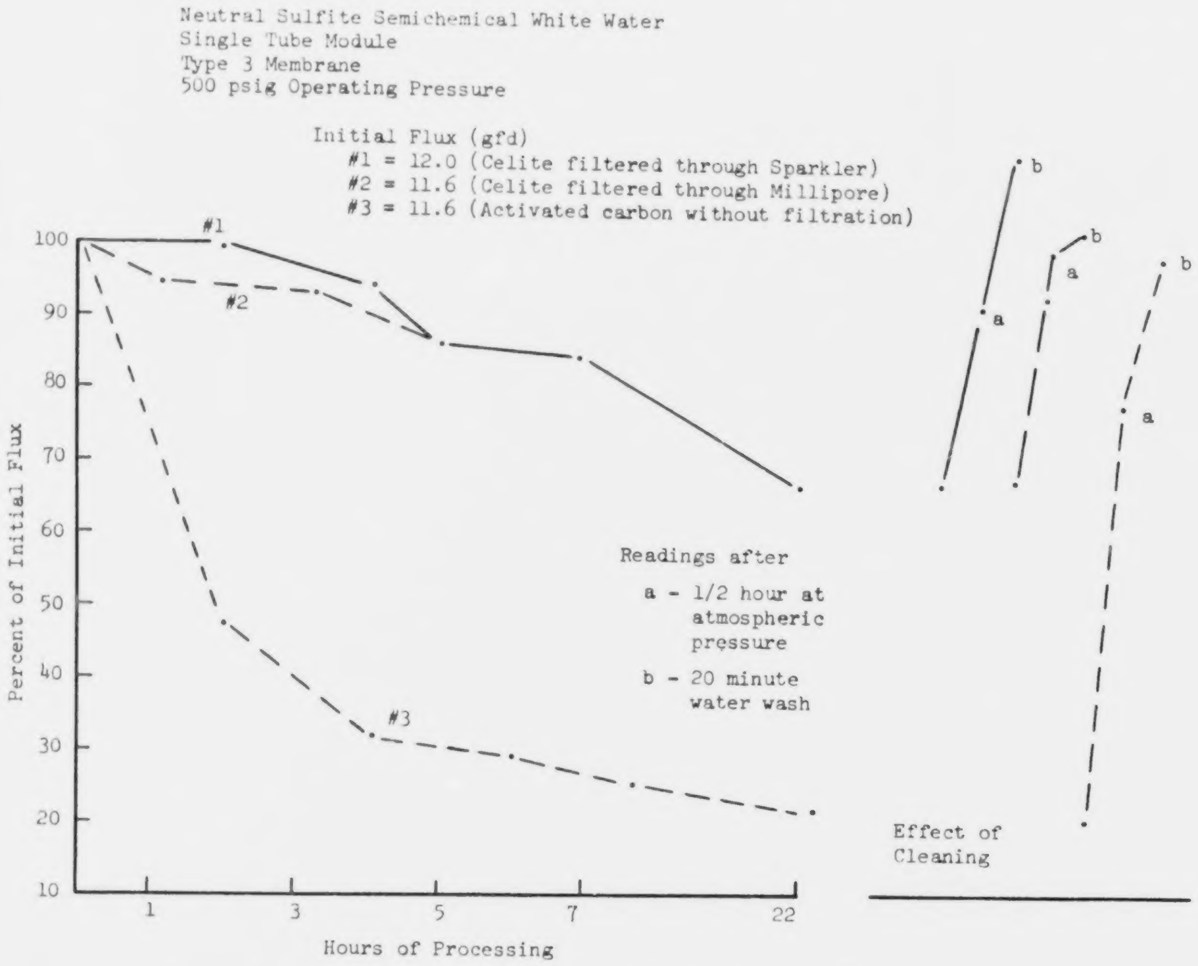


Figure 6. Attempts to Remove Foulant with Adsorbants — Effect on Flux Loss

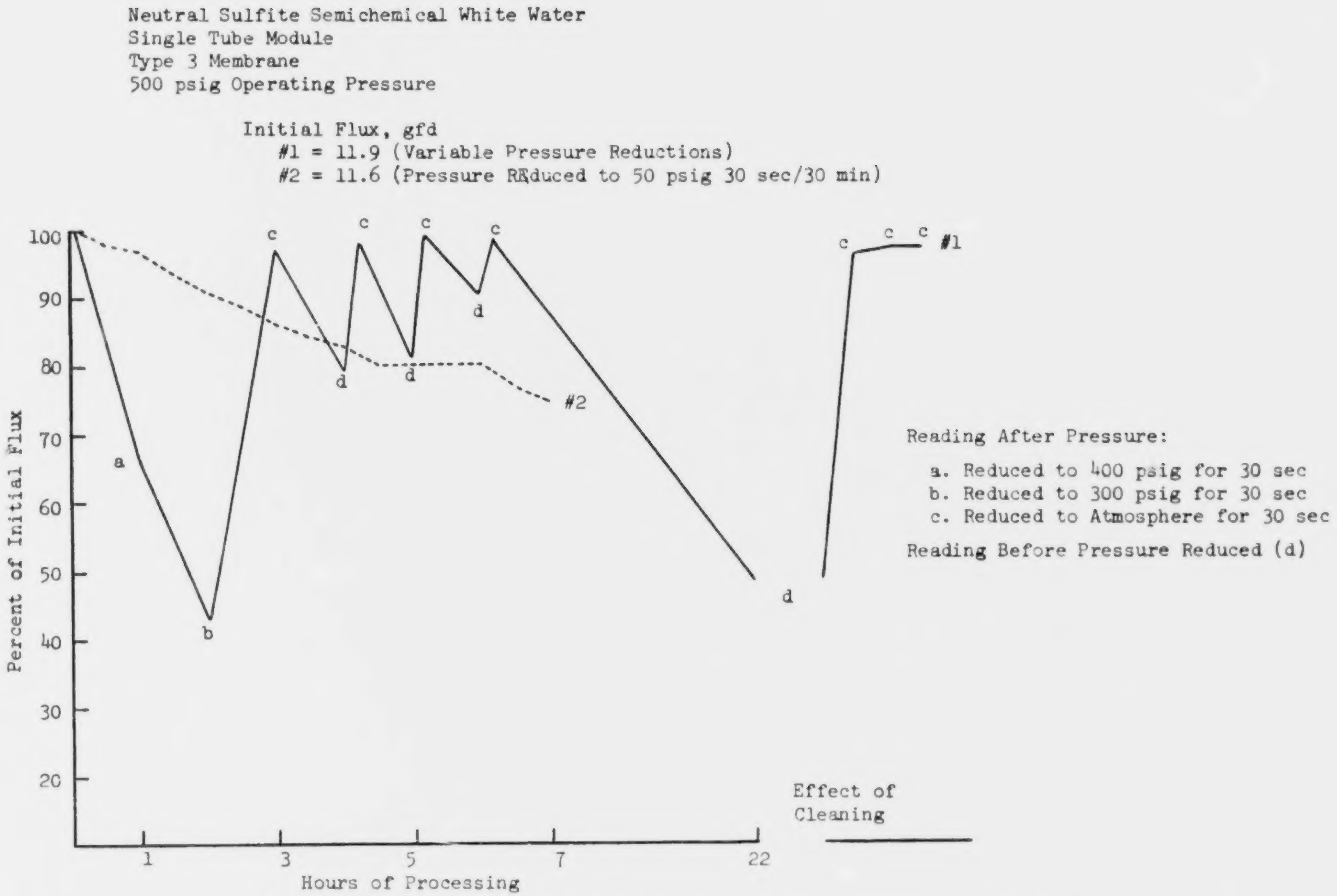


Figure 7. Effect of Sudden Reductions in Operating Pressure on Flux Loss

The following curves illustrate the research phases in the development of "pressure-pulsing" and an attempt to detail some of the variables that might be used with different processes to maintain high water production during sustained operation.

Figure 7. The effectiveness of reduction in operating pressures (500 psig) to 400, 300, or to 50 psig in maintaining flux rates was studied by partially opening the bypass valve between the pump and the modules (the relief valve in Fig. 5) for 30 seconds at regular intervals. This produced not only a reduction in the pressure, but at the same time a drop in fluid flow through the modules. Pressure reductions on the order of 100-200 psig failed to maintain a high flux. Reductions to 50 psig also failed to eliminate declines in the flux rate but did markedly decrease the rate of flux loss.

Figure 8. With provision for complete depressurization, periodic pressure reductions (pulsations) to atmospheric pressure levels by opening the relief (bypass) valve between the pump and the modules, resulted in maintaining an average flux level between 95 and 103 percent of the initial flux rate (Curve 1). Reductions in the pressure produced by opening a valve between the modules and the regulating valve (Modification 1 on Fig. 5) resulted in pressure reduction, and at the same time a very rapid increase in the velocity of fluid through the modules as the accumulator discharged its volume of fluid. While this "washing" had little apparent effect on the overall flux rate, there was evidence that the variations in flux rates were greater (Curve 2).

Since flux values plotted in Curves 1 and 2 of Fig. 8 were from readings after pressure-pulsing, we had no data on the flux rates between readings; i.e., the "low" values obtained during each 30-minute period. A trial was made to determine the fluxes before and after the pressure reductions. Results of this study (Curve 3) demonstrate flux variations between 5-8 percent of the initial value for 30-minute cycles between depressurizations and an increase in the magnitude of the variations when the processing time between "pulses" was increased.

Further studies with automatically timed, rapid opening ball valves in-line between the module and the pressure regulating valve (Modification 2 in Fig. 5) and 40, 80, and 100-minute pressure-pulsing cycles resulted in maintaining flux levels between 90-100 percent of the initial during sustained operations (Fig. 9)

Extension of these studies to single and multimodule installations have resulted in several additional modifications of the pressure-pulsing procedure. In certain waste streams the pressure pulsing cycle can be as long as 4 to 6 hours, while in others a shorter cycle may be required to maintain optimum flux rates.

During the pressure reduction cycle, a back-flow of permeate was observed, and this is believed to permit "osmotic" rinsing of the membrane. It

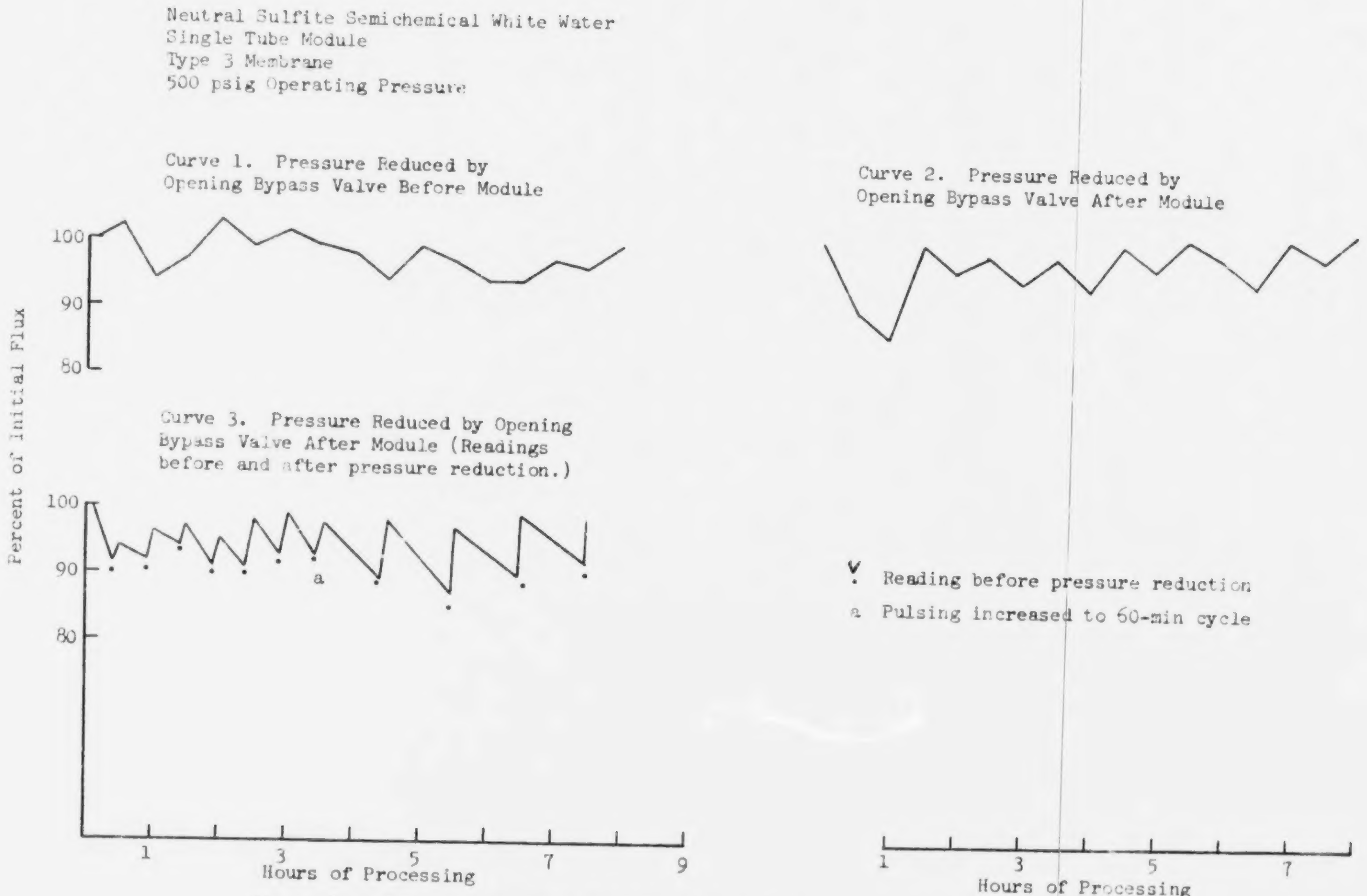


Figure 8. Effect of Pressure Pulsing at Various Points in RO System on Flux Loss

Neutral Sulfite Semichemical White Water
Single Tube Module
Type 3 Membrane
500 psig Operating Pressure
Initial Flux Rates = 6.4 gfd

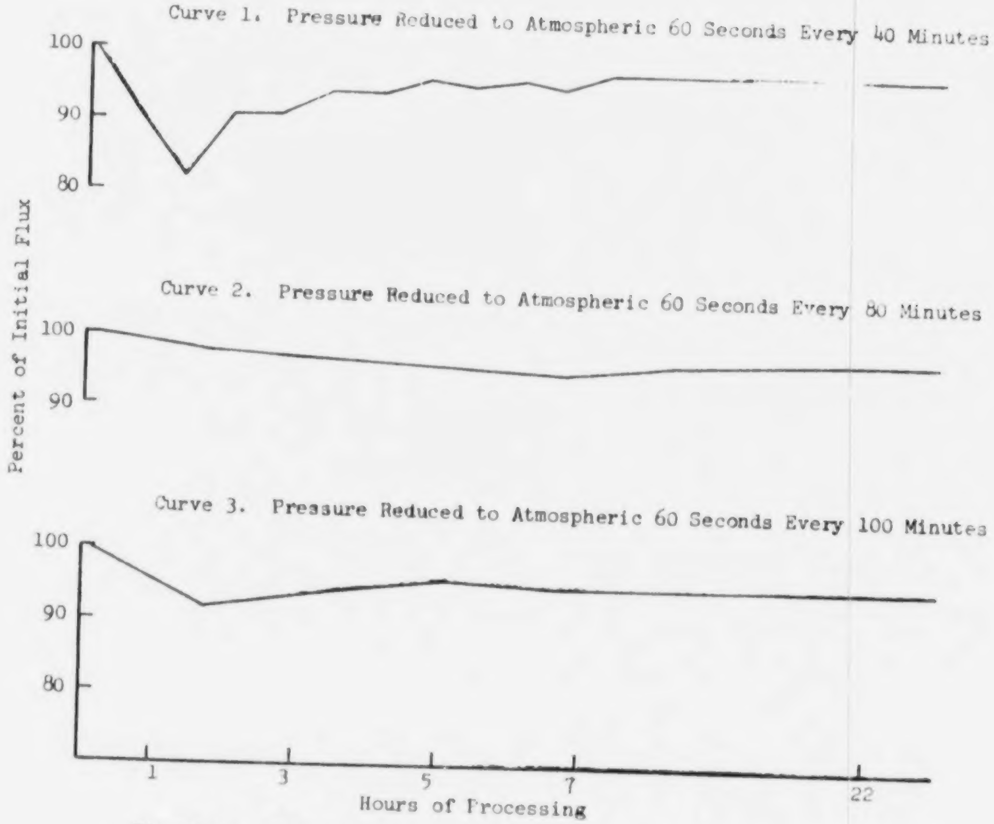


Figure 9. Effect of Pressure Pulsing Cycle Rate on Flux Loss

is necessary to maintain the permeate discharge lines submerged in a vessel containing sufficient permeate so as to keep the modules filled during this back-flow cycle.

In additional laboratory and field trials, we found that a rapid depressurization of the system (from operating pressure to atmospheric) was more effective in restoring the flux rate than was a slow pressure reduction coupled with flow stoppage; these procedural modifications have been termed "hard" and "soft" pressure pulsing, respectively. However, the capabilities of membrane support structures to withstand the added stress of hard pulses has been a question yet to be resolved. Much experience has been gained in some four years of testing, but this must be recognized as a difficult design and manufacturing problem. High velocity is considered to be at least a partial alternative to hard pulsing.

Additives

During the period of development of the mechanical method for maintaining clean membrane surfaces, a study was also being undertaken to chemically block the deposition of "fouling agents" by the addition of various dispersants and other fouling depressants to the feed stream.

The use of additives, such as cationic polymers, ethylenediamine tetraacetic acid (EDTA), aryl alkyl sulfonates and polyphosphates showed little promise of inhibiting membrane fouling (Table 11). High levels of these additives at excessive cost were indicated to be required for significant reductions in fouling effects.

Chemical Cleaning

Module cleaning procedures, which included washing with chemicals, such as EDTA, detergents, fractionated liquor products, acid or alkali solutions, and enzymatic laundry detergents did show promise for removing fouling agents from the surfaces of the membranes (Table 12).

In the concentration of a calcium acid sulfite wash water from 1 percent solids to 10 percent solids, a precipitation and deposition of calcium sulfate (or sulfite) was often encountered. By careful control of the concentration levels, velocity, and other operating parameters the deposition of this scale material could be minimized or eliminated. If, however, the membranes did become coated with calcium salts, a wash with a 1 percent solution of EDTA removed the material and restored the flux rate if the scale had not been allowed to dry or become heated to form the dehydrated salt.

In most of the other processing test runs a flush with a 1.5 percent solution of an enzymatic detergent (BIZ) for 20 minutes, followed by a rinse with pH 3 water to remove the alkaline detergent, has proven adequate for restoring the flux.

TABLE 11

STUDY OF MEMBRANE FOULING WITH A SINGLE-TUBE HAVENS MODULE USING ADDITIVES TO PREVENT FOULING

Kraft Pulp Wash Water
500 psig Operating Pressure
pH 7.0 Temperature 35-40°C

Hours of Operation	Flux Rate, gfd at 40°C
No additive (control)	
1	14.4
7	9.6
22	5.2
Added 25 mg/l Polytergent B-300	
1	13.5
7	11.4
22	7.7
Added 50 mg/l Polytergent B-300	
1	13.5
3	13.5
5	13.5
23	11.8
Added 75 mg/l Polytergent B-300	
1	14.4
3	14.0
6	14.4
22	12.7
29	10.9

Hours of Operation	Flux Rate, gfd at 40°C
Added 10 mg/l Versene-100 (EDTA)	
1	14.8
2	14.0
18	9.2
Added 25 mg/l Versene-100 (EDTA)	
0.5	14.0
2	13.5
5	13.1
21	9.2
Added 100 mg/l Versene-100 (EDTA)	
1	14.4
5	14.0
6	14.4
22	11.8

Pulsonic Cleaning

The use of high velocity water at elevated, "vibrating" pressure, similar to that used for automobile washing and airplane de-icing, was explored briefly as a method for the cleaning of fouled modules. The results were somewhat inconclusive. Single modules did appear to be cleaned in this way but multiples of several modules showed little effect. The possibility of damaging expensive modules halted further trials.

Concentration Studies on Other Pulp and Paper Mill Effluents

A substantial number of dilute pulp and paper waste streams have been successfully concentrated when employing suitable modifications of the basic RO process. These include not only acid sulfite, neutral sulfite, and kraft liquors, wash waters, and bleach effluents discussed in preceding sections of this chapter, but also the following waste streams:

TABLE 12

STUDY OF MEMBRANE FOULING WITH A SINGLE-TUBE HAVENS MODULE
CLEANING PROCEDURES AFTER FOULING

Kraft Pulp Wash Water
500 psig Operating Pressure
pH 7.0 Temperature 35-40°C

Hours of Operation	Flux Rate, gfd at 40°C
No Pretreatment	
0.5	18.9
2.5	18.5
5.5	17.0
22	13.1
30	11.1
46	8.4
50	8.4
Washed with 2 Percent Polytergent B-300	
52	9.4
68	6.9
Washed with 2 Percent Versene-100 (EDTA)	
69	18.5
70	19.1
No Pretreatment	
0.5	18.9
22	9.2
Washed with 1/2 Percent Versene-100	
23	15.7
Washed with 1 Percent Versene-100	
25	17.5
Washed with 2 Percent Versene-100	
27	18.9
Washed with 1.5 Percent BIZ (enzymatic detergent)	
29	18.8

Hours of Operation	Flux Rate, gfd at 40°C
No Pretreatment	
1	14.4
22	5.2
Washed with 2 Percent Aldonolig (Fraction of SSL)	
23	7.4
Washed with 5 Percent Aldonolig	
24	11.4
Washed with 2 Percent Versene-100	
26	14.7
No Pretreatment	
1	16.2
22	7.9
Washed with 5 Percent Aldonolig	
25	12.2
Washed with 2 Percent Polytergent B-300	
27	12.2
Washed with 2 Percent Versene-100	
29	16.4
No Pretreatment	
1	15.9
22	7.1
Washed with 1.5 Percent BIZ (enzymatic detergent)	
23	15.7
Washed with 2 Percent Versene-100	
24	15.7

Hypochlorite Bleach Effluent

A calcium hypochlorite bleach effluent was processed in one of the small laboratory units using Type 3 membranes in tubular modules at flux rates of 6-9 gfd and rejections of 81 percent for solids, 78 percent COD, and 74 percent for chlorides (Table 13).

TABLE 13

PROCESSING OF HYPOCHLORITE BLEACH PLANT EFFLUENT BY REVERSE OSMOSIS WITH PRESSURE PULSING

Havens single-tube module
Type 3 membrane
600 psig Operating pressure
Pressure pulsing 30 sec/30 min

Stream	Solids, mg/l	COD, mg/l	Chloride, mg/l
Feed	2726	491	673
Product water	521	106	172
Rejection, percent	81	78	74

Flux rates = 6-9 gfd.

The rather low values for both flux rate and rejections reflect the higher inorganic salt content having high osmotic pressure. In field tests, without pressure pulsing, scaling of the membrane surfaces with a material which analyzed 19.3 percent calcium and 37.4 percent ash was encountered. While the fouling agent was organic in character, there was evidence that calcium deposits were aggravating the problem. This was substantiated by the ease with which the membrane surfaces could be restored by flushing with a solution of EDTA.

A second trial with the same waste as used for the field test, but with pressure pulsing, was successful in removing 90 percent of the water without a marked decline in the flux rates other than the decline to be expected with the increased osmotic pressure (Table 14).

Barking Waters

The removal of bark from pulp logs prior to chipping for the making of pulp requires large quantities of water and results in a waste stream having a dilute suspension of fine particles and dissolved substances.

TABLE 14

RO CONCENTRATION OF A HYPOCHLORITE BLEACH EFFLUENT WITH PRESSURE PULSING

Single-tube Havens module
Type 3 membrane
600 psig Operating pressure
Pressure pulsing 30 sec/hour

Stream	Water Recovery, percent	Flux, gfd	Solids, mg/l	COD, mg/l	Chloride, mg/l
Tap water		16.6			
Feed			3010	502	677
Product water					
1	40	10.1	120	20	206
2	60	8.7	148	40	220
3	90	6.5	157	43	222
Concentrate			28650	4633	4722
Tap water		16.1			

A test sample of a barking water which had been clarified by screening and sedimentation was successfully concentrated by RO to about 2.0 percent total solids and an almost odorless product water with 71 mg/l dissolved solids, zero suspended solids and no measurable color (Table 15) was also produced.

Concentration to a solids level which could be utilized by burning (or other disposal) equipment could require the removal of 99-99.8 percent of the water. Technically this appears possible but the economics of such high levels of concentration have not appeared favorable. Special conditions may alter this situation and permit development of practical applications.

Deinking and Other Paper Recycling Waste Waters

In the recycling of paper there are process effluents from deinking of printed paper and cleaning of fibers from coated clay-filled paper, which have critical disposal problems not yet completely solved. Highly colored paper machine white waters have been successfully processed in the laboratory RO systems at high flux rates using Type 2 (open) membranes with unexpectedly high rejections of solids (90 percent), COD (97 percent), color (99+ percent), and phosphates (96 percent) (Table 16). The high phosphate rejection could also be of importance in processing other phosphate-containing effluents from the pulp and paper industry. It is probable that use of the tighter, Type 3 membrane would raise the rejection of the phosphates to the order of 98 percent or better.

TABLE 15

REVERSE OSMOSIS PROCESSING OF BARKING WATER

Spiral wound module
Type 4A-2 membrane
450 psig Operating pressure

Stream	Water Recovery, percent	Flux Rate, gfd at 40°C	Solids, g/l	Optical Density at 281 nm[a]
Feed			0.370	1.36
Product water				
1	60	7.2	0.042	0.184
2	80	7.8	0.050	0.219
3	90	8.2	0.071	0.279
Concentrate			1.98	7.20

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[a] A measure of the lignin content.

TABLE 16

PROCESSING OF DEINKING WASTES BY REVERSE OSMOSIS

Single-tube module
600 psig Operating pressure
Pressure pulsing 30 sec/30 min

Stream	Solids, mg/l	COD, mg/l	PO_4, mg/l
Feed	3870	2240	17.7
Product water	389	123	0.68
Rejection, percent	90	94.5	96.2

Initial product water flux = 16.3 gfd.
Flux range for 8-hour run = 15.7-16.4 gfd.
Final product water flux = 16.4 gfd.

Paper Coating Effluents

A study was also made of the possibility of concentrating paper coating effluents for reuse. A test was undertaken with a starch-filler-brightener material from a coating operation. Titanium dioxide (white) and clays were the chief components in the feed liquor.

Using the reverse osmosis process, with the pressure-pulsing modification, concentration of these waste streams with tubular modules was carried out with manually controlled pressure reductions of 30 seconds per hour (Fig. 10). Overnight, unpulsed, operation and cleaning steps are included to show the flux losses without pressure pulsing and methods that can be used to reestablish the water transport rates.

Products #3 and #4 and a mixture of all four products (#1-4), were successfully concentrated with flux rates on the order of 85-101 percent of the initial values as long as the pressure pulsing schedule was maintained and to 70 percent of the initial if "pulses" were discontinued overnight.

Products #1 and #2, which contained large percentages of alum, had fluxes which decreased throughout the run, even with pressure pulsing at 30 seconds per hour. An increase in the pulsing cycle to half-hour intervals might have decreased the flux declines, but this has not been investigated.

Evaporator Condensates

Early in 1966 studies were conducted on RO processing of the condensates from two different evaporator systems. Observations at that time were:

1. Ninety to ninety-five percent of the water could be recovered from an acid sulfite condensate as a colorless, odorless product with high electrical resistance (low concentrations of ionizable components).

2. Sixty percent of the water could be recovered with a 3-fold reduction in both Chemical Oxygen Demand (COD) and Volatile Acids (VOA), but there was a marked increase in the transport of materials contributing to the COD and VOA content of the permeate water as the concentration and water recovery continued above the 60 percent level.

3. The product water and concentrate pH and resistance values indicate that the main constituents of the product waters were organic acids and those of the concentrate were inorganic salts and ligninlike materials with "high color" (Table 17).

A substantial program of laboratory study was undertaken with these condensates since they comprise a major proportion of the BOD_5-load remaining in total pulp mill effluents after disposal processing of the digester liquors has been undertaken. These studies included:

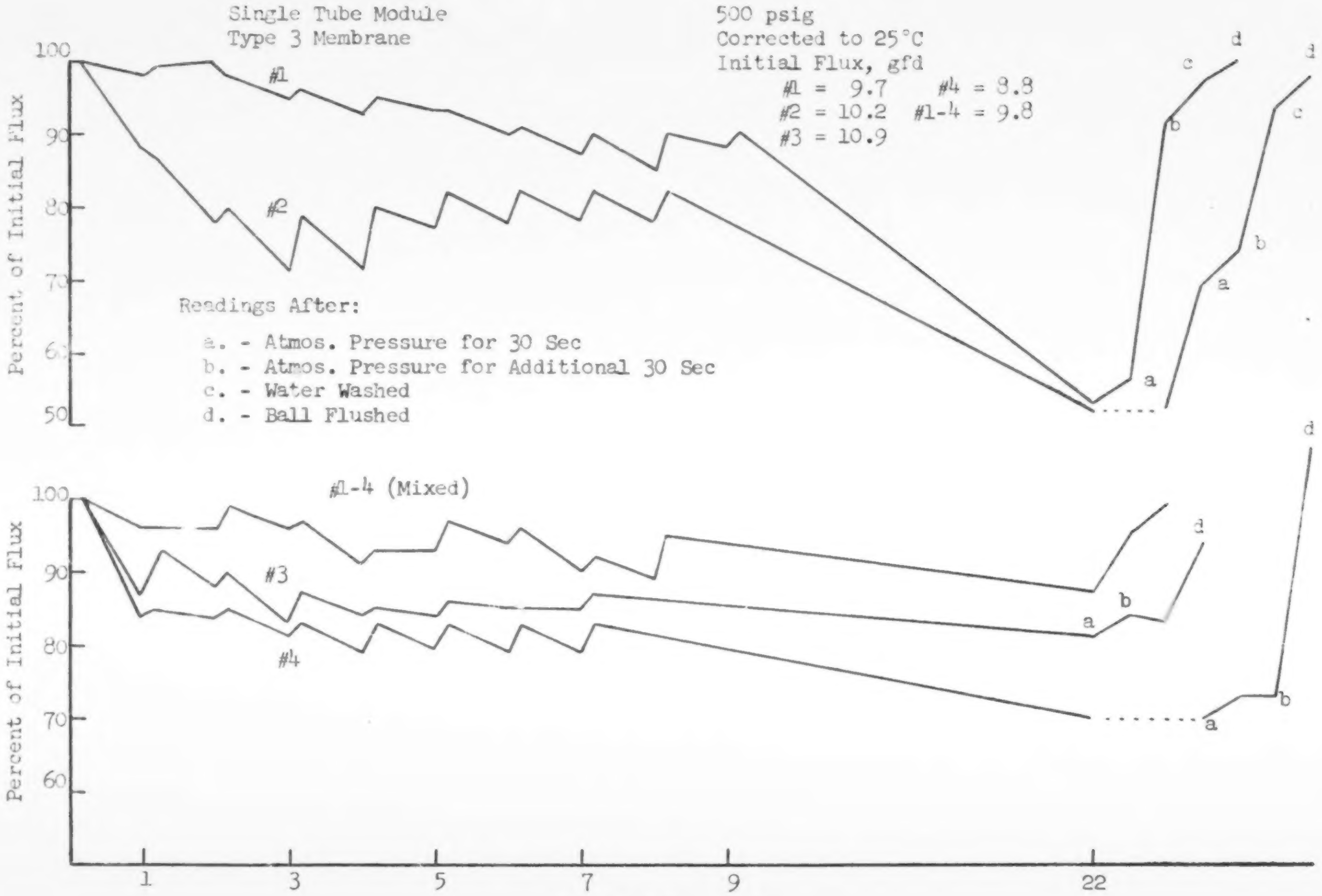

Figure 10. Processing of Coating Effluents by Reverse Osmosis

TABLE 17

REVERSE OSMOTIC PROCESSING OF EVAPORATOR CONDENSATES

Spiral Wound Module
5A-2 (Old-Dense) Membrane
450 psig Operating Pressure

Product Water Recovery, percent	Volume, liters	Total Time, hours	Resistance, ohm-cm	Flux, gfd	pH	Total Grams Vol. Acids	Total Grams COD
Aqua-Chem Evaporator							
Feed	100		330		4.0	299	790
60	60	18.9	3158	3.0	4.0	96	280
75	75	24.3	2973	3.0	4.1	--	395
99	99	35	2652	2.9	4.2	139	547
Conc.	1		38		5.2	15	41
Rosenblad Evaporator							
Feed	100		220		4.0	341	394
60	60	23.3	2431	2.8	3.6	100	107
70	70	27.3	2323	2.8	3.6	155	143
95	95	40	2062	2.8	3.8	208	214
Conc.	5		66		3.8	38	115

1. The effects of operating pressure on rejection (Table 18).

2. Stripping to remove the sulfur dioxide followed by processing with and without pH adjustment (Table 19).

3. The adjustment of the pH to 7.0 and processing at four levels of solids concentration (Table 20).

4. Processing of acetic acid solutions in a hollow nylon fiber module (above studies were with tubular systems) at higher pH levels than could be used in the cellulose acetate designs (Table 21 — Fig. 11).

5. And finally sustained operation with the spiral wound modules for continuous concentration of an acid sulfite condensate at pH 6.0-6.8 (Table 22).

TABLE 18

REVERSE OSMOSIS PROCESSING OF ACID SULFITE EVAPORATOR CONDENSATE AT TWO PRESSURE LEVELS

Seven-Tube Module
Type 3 Membrane

Sample	Water Recovery, percent	Flux, gfd	Volatile Acids g/l	pH
450 psig (pH Adjusted to 5.0 with NaOH)				
Feed			14.7	5.0
Product Water				
1	40	5.5	3.88	4.0
2	60	5.7	4.06	3.9
3	80	5.5	4.17	3.0
Concentrate			44.84	5.4
250 psig (pH Adjusted to 5.0 with NaOH)				
Process Feed			15.6	4.9
Product Water				
1	40	3.0	4.17	3.8
2	60	3.0	4.44	3.8
3	80	2.4	4.29	3.9
Concentrate			32.20	5.2

TABLE 19

REVERSE OSMOSIS PROCESSING OF MAGNEFITE EVAPORATOR CONDENSATE

Spiral wound module
Type 4A-2 membrane
450 psig Operating pressure

Sample	Water Recovery, percent	Flux, gfd	Solids, g/1	Volatile Acids, g/1	pH
As Received					
Process feed			8.62	5.11	1.65
Product water					
1	60	6.0	7.84	4.11	1.75
2	80	10.9	7.54	4.02	1.75
3	90	12.2	7.89	4.97	1.72
Concentrate			11.28	10.69	1.58
pH Adjusted with NaOH					
Process feed			11.55	4.66	6.61
Product water					
1	60	5.0	7.47	2.20	6.69
2	80	6.8	7.39	2.24	6.71
3	90	7.5	8.57	3.57	6.70
Concentrate			29.40	12.64	6.65
Steam Stripped only					
Process feed			4.51	4.25	2.85
Product water					
1	60	11.7	4.29	3.85	2.82
2	80	11.5	4.30	3.89	2.85
3	90	12.2	4.70	4.24	2.82
Concentrate			5.20	6.22	2.78
Steam Stripped & pH Adjusted with NaOH					
Process feed				4.76	
Product water					
1	60	6.4		3.36	
2	80	6.8		3.74	
3	90	6.1		5.18	
Concentrate				14.13	

TABLE 20

REVERSE OSMOSIS CONCENTRATION OF AN ACID SULFITE EVAPORATOR CONDENSATE WITH pH ADJUSTMENT OF THE FEED

18-Tube module
600 psig Operating pressure

Rejection = 1 - C_p/C_f

Concentration, g/1 solids	pH Feed	Type 3 Membrane							Type 5 Membrane						
		Solids	OD	BOD	COD	NH_3	Conductivity	Volatile Acids	Solids	OD	BOD	COD	NH_3	Conductivity	Volatile Acids
8	2.7	0.27	0.66	0.26	0.19	0.34	0.58	0.07	0.45	0.79	0.42	0.37	0.72	0.69	0.26
	4.8	0.57	0.55	0.45	0.43	0.34	0.65	0.40	0.81	0.74	0.62	0.62	0.78	0.95	0.70
	6.1	0.70	0.48	0.58	0.57	0.34	0.70	0.65	0.96	0.90	0.82	0.81	0.72	0.90	0.95
14	3.2	0.45	0.81	0.39	0.41	0.57	0.72	0.22	0.63	0.86	0.54	0.54	0.74	0.91	0.40
	4.3	0.57	0.66	0.53	0.53	0.57	0.69	0.47	0.84	0.85	0.73	0.71	0.80	0.96	0.70
	7.0	0.75	0.62	0.63	0.60	0.48	0.61	0.68	0.97	0.87	0.87	0.84	0.70	0.97	0.97
19	3.0	0.53	0.73	0.43	0.49	0.63	0.78	0.23	0.78	0.84	0.63	0.62	0.82	0.92	0.40
	4.8	0.63	0.69	0.55	0.59	0.67	0.75	0.50	0.91	0.84	0.79	0.77	0.83	0.97	0.73
	6.5	0.70	0.57	0.67	0.62	0.65	0.73	0.68	--	0.80	0.86	0.84	0.77	0.98	0.98
28	3.5	0.67	0.69	0.69	0.54	0.72	0.80	0.26	0.80	0.87	0.82	0.69	0.86	0.95	0.45
	5.4	0.74	0.66	0.72	0.63	0.61	0.74	0.60	0.96	0.88	0.83	0.86	0.86	0.98	0.85
	6.8	0.72	0.54	0.68	0.59	0.63	0.75	0.56	0.97	0.76	0.81	0.85	0.79	0.99	0.98

	Concentrations in Feed						
	g/1	Pt	mg/1	mg/1	mg/1	ohm cm	g/1
8	8	110	5400	7500	18	158	4.2
14	14	280	9700	13400	35	90	4.7
19	19	500	10300	16600	60	76	6.3
28	28	690	11700	23000	72	52	8.1

TABLE 21

REJECTION OF ACETATE IONS AT VARIOUS pH LEVELS

Hollow fiber module (No. 1)
Acetic acid solution - 5 g/l

pH	Sample	Conversion, percent	Rejection, percent Range	Rejection, percent Average	Feed Pressure
3.0	P-1	12.8	23.3		360
	P-2	13.0	12.2		360
	P-3	13.2	8.7		360
	P-4	13.5	11.0		360
	P-5	13.8	10.7		358
	P-6	14.0	13.4	11	358
4.0	P-1	13.1	28.0		363
	P-2	13.2	20.9		362
	P-3	13.4	21.1		361
	P-4	13.5	21.1		360
	P-5	13.6	20.5		362
	P-6	14.1	21.1	21	362
5.0	P-1	12.9	57.2		365
	P-2	12.9	47.5		366
	P-3	13.0	47.3		364
	P-4	13.2	46.8		362
	P-5	13.1	46.8		364
	P-6	13.2	47.3	47	365
6.0	P-1	11.7	74.6		361
	P-2	11.8	73.2		360
	P-3	12.1	73.0		360
	P-4	12.0	72.1		360
	P-5	12.0	73.0		360
	P-6	11.9	72.7	73	360
8.0	P-1	11.9	85.4		360
	P-2	11.9	82.0		360
	P-3	12.1	79.8		362
	P-4	12.1	82.0		361
	P-5	12.2	83.8		361
	P-6	12.2	81.3	82	361
11.0	P-1	13.0	84.4		340
	P-2	12.6	82.3		341
	P-3	12.6	83.2		341
	P-4	12.7	89.0		341
	P-5	12.8	84.4		341
	P-6	13.0	88.1	85	341

$$\text{Percent Conversion} = \frac{\text{ml permeate x 100}}{\text{ml permeate + ml reject}}$$

$$\text{Percent Rejection} = 100\left(1 - \frac{C_p}{C_f}\right) \quad C_p = \text{Conc. permeate} \quad C_f = \text{Conc. feed}$$

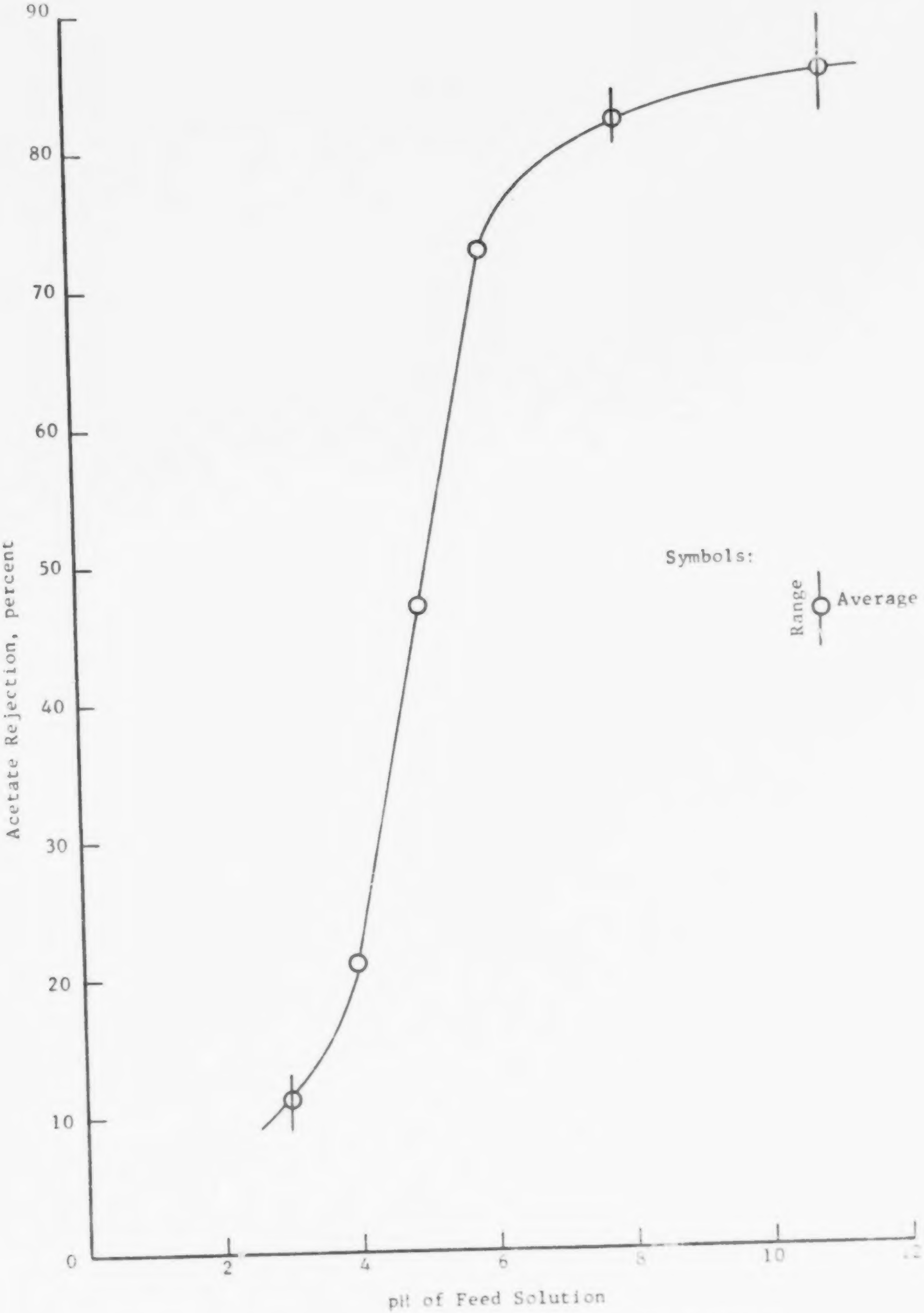

Figure 11. Effect of pH on Acetate Ion Rejection

TABLE 22

REVERSE OSMOSIS PROCESSING OF A CALCIUM-BASE ACID SULFITE EVAPORATOR CONDENSATE AFTER pH ADJUSTMENT

Spiral wound modules
pH Adjusted with NaOH
600 psig Operating pressure
3 gpm Flow rate

System Flow Pattern	Percent Solids Concentration	Percent Water Removal	Rejection, percent			Flux Rate, gfd
			BOD_5	VOA	COD	
Straight through at pH 6.7	0.48 to 0.51	5.7	77.4	95.0	88.4	8.3
Recycle for concentration at pH 6.4	0.55 to 2.46	78.0	98.6	95.6	91.3	4.2
Recycle for concentration at pH 6.0	0.39 to 5.59	93.0	92.8	96.0	96.4	2.1

The studies were conclusive in showing membrane systems available for the study on this project were not capable of rejecting low molecular weight organic acids such as acetic, inorganic acid volatiles such as SO_2 and also organic neutrals such as methanol. Conversion of the acid volatiles to salt forms altered the rejection capabilities and this neutralization route remains an interesting possible method of effectively processing pulp mill evaporator condensates by membrane concentration. However, the expense of neutralization is high, and this membrane route is unlikely to be widely used for disposal processing but rather for recovery of values whenever a market can be developed with a return sufficient to balance the neutralization and subsequent concentration costs in competition with synthesis of acetic acid and related volatiles from petroleum sources. Other, more economic routes to disposal processing of this waste flow are being sought and the future of not a few of the older acid sulfite pulp mills hinges on successful outcome of this overall research effort toward practical routes for disposal if not for utilization.

SECTION VI

DESIGN OF THE LARGE-SCALE TRAILER UNIT FOR REVERSE OSMOSIS CONCENTRATION OF PULPING PROCESS EFFLUENTS

The review and discussion in this section extends upon a prior publication[7] describing the development of the engineering design for large-scale applications of reverse osmosis (RO) as a method for concentrating dilute wastes without phase change. In this modification of RO for pollution control and effluent treatment, the water contained in relatively dilute process streams is forced under pressure through a membrane in conventional RO modules originally designed for salt water conversion applications. However, the objectives for this demonstration program called for a much higher degree of water recovery ranging from 70 percent to more than 95 percent of that contained in the dilute feed waters and also for much higher concentrations of the dissolved solids rejected by the membrane system than is normally practiced in salt water and brackish water conversion. This points to a growing need for designing membrane systems especially to meet the requirements for concentrating systems. This is indeed taking place, and much ingenuity is apparent in equipment designs becoming available from suppliers. The choice of tubular membrane systems from among the available RO conformations has been described in the foregoing pages as a necessary first step in planning the large-scale demonstration studies and design of the large field unit.

The degree of feed pretreatment required, the quality of the concentrate, and of the water permeate become matters of added concern, since these products are to be subject for reuse or for final disposal without pollution of the water, land, or air environment.

Considerable time and effort in the Effluent Processes Group laboratories of The Institute of Paper Chemistry has been directed to investigation of the potential applications of the RO process for concentrating the dilute effluents of the pulp and paper industry as a preliminary justification for these more detailed studies on design of the field unit. Those preliminary studies developed the basic information for planning the program of application studies for the research and demonstration grant as described in the various following sections of this report. The data developed in this section were the next step toward design, construction, and operation of the large trailer-mounted field demonstration unit for processing specific waste streams at individual pulp mills at feed rates in the range of 20,000 to 100,000 gallons daily.

The development of the principal and more important design criteria followed studies in several areas of engineering evaluation.

Selection of specific types of RO equipment

Module configuration

Type of membrane

Methods of feed pretreatment

Development of membrane flux rate and rejection parameters for unit design

Hydraulic parameters for design of the system

Velocity of flow across the membrane

Pressure drop

Final development of the flow sheet and detailed design of the unit

SELECTION OF REVERSE OSMOSIS EQUIPMENT

One of the first questions to be answered when designing a reverse osmosis unit concerns the selection of module configuration and the type of membrane to be used. The selection of module design is an important factor from the standpoint of membrane fouling whereas selection of the type of membrane is affected by the nature of the effluent water; the required pretreatment of the feed; and the rejection characteristics of various components contained in the feed. The selection of module design and of the type of membrane are discussed separately below.

Module Design

The configurations of RO equipment available at the time of initiating these design studies included:

Tubular Design

A number of suppliers have for the past 10 years been progressing in development of tubular membrane support configurations based upon tubes constructed of molded or extruded resins, resin-bonded glass fiber, solid or perforated metals, and more recently a design with tubes supported and surrounded in resin bonded sand or other aggregates. The tubular systems provide for clean hydraulic flows at high velocities which have proved to be advantageous for concentrating effluents containing suspended particles. Colloidal solutions and true solutions which throw down precipitates or crystalline scale-forming deposits on concentration are advantageously processed in the tubular design.

Tubular designs may have ratios of membrane surface to module volume in the 50 to 200 square feet per cubic foot range, which is relatively low in comparison to other configurations and handicaps the competitive development of low cost modular systems accordingly. However, this disadvantage can be outweighed by the basic hydraulic operating credits of a well-designed tubular system.

Spiral Wound Modules

The "jelly roll" configuration of the spiral wound module design provides much more membrane area per unit of module volume than can be had for tubular designs having the usual inside diameters in the range of 1/4 to 2 inches. This advantage of the spiral wound design can be on the order of 10 to 100 times that of the tubular equipment, and the cost advantage is significant and well developed for processing clear brackish waters and the like which are free of suspended matter and which do not throw down precipitates or crystalline deposits during concentration. However, the experience in preliminary studies of pulping effluents as previously described indicated the tolerance for even small quantities of suspended matter to be critically low for the spiral designs available for laboratory and field phases of this study in 1968-69.

Hollow Fiber Configuration

This configuration is still more advantageous in terms of the high ratio of up to 10,000 square feet of membrane surface per cubic foot of module volume. But the even greater sensitivity of the bundles of microfibers to plugging with suspended matter has proven to be a substantial roadblock to large-scale application studies to concentration processing of the dilute industrial effluents covered in this report.

Type of Membrane

The commercial production of RO equipment at the time of design and construction of the trailer unit was still in relatively early stages of development. The membrane modules available on the market were designed for operating in the range of 500 to 1000 psig, but relatively little data were yet available in terms of module life and performance based upon sustained continuous operation.

RO equipment commercially available has been almost exclusively based upon two types of membranes - cellulose acetate and nylon, and upon various modifications in the formulation and casting of those membranes. The rate of hydrolysis for cellulose acetate, as reported in the literature, has been reported to be lowest at a pH of about 4.5. Deterioration of cellulose acetate membranes accelerates as the pH ranges above or below this point. For most applications, a lower pH limit of 2.5 to 3.0 and an upper limit of 7.0 to 8.0 seems to be acceptable. Nylon membrane systems can stand feed solutions of pH 2.0 to 12.0, and therefore might be selected for processing solutions in a broader range of applications to reduce the need and the expense for neutralization of acidity or alkalinity.

Operation at the pH level of the feed solution as received may reduce the problems arising from membrane fouling. This reduced level of membrane fouling seems to be due to the fact that most feed liquors tend to be in a state of equilibrium at a particular pH, but if the pH is changed, the chances for precipitation, scale formation, and the like, increases and may result in fouling of the membrane.

In addition to the pH effect, the deterioration of the membrane is also affected by higher temperatures of solution. For both cellulose acetate and nylon membranes, an upper limit of 40°C has usually been specified by the membrane manufacturer.

The flux rate and rejection characteristics of a membrane can be varied over a fairly wide range, depending substantially upon the "tightness" of the membrane. These operating characteristics may in the case of cellulose acetate be substantially controlled by the degree of heat treatment and in the solvent formulation used in fabrication of the membrane.

In the pulp and paper industry, most of the dilute wastes contain low molecular weight organics, such as wood sugars, which affect the BOD and COD. Removal of a minimum of 75 percent of those components requires a fairly tight membrane. Different types of 1/2-inch tubular modules having cellulose acetate membranes were tested. Those with rejection performance similar to Havens Type 3 membrane proved to be the most satisfactory of those available in 1968-1969. Tests covered the range equivalent to Havens coarse Type 2 to very tight Type 5 membranes. Other manufacturers had membranes with a similar range, but with proprietary differences in their individual numerical designations of types and grades. Specifications established for the trailer unit called for performance equivalent to 7000 square feet of membrane with moderately tight rejection capabilities equivalent to the No. 3 membrane.

PRETREATMENT OF FEED

Pretreatment of feed is important from the standpoint of membrane-module life, and in maintaining steady long-term flux rates with minimum loss of operating time for shutdowns and washups of the system. For the tubular cellulose acetate modules finally selected, planning called for minimum levels of pretreatment to maintain temperatures in the range of 20 to 40°C and pH levels between 3.0 and 7.0. Gross quantities of pulp fiber occasionally escaping into the feed and which could accumulate and plug check valves and gages were to be taken care of by passing the feed through a 100-mesh screen. This may be finer than actually necessary since a more coarse 40-mesh appeared fully adequate in later tests during Demonstration No. 2 on NSSC liquor. A side hill screen proved adequate in some of these studies but, in others, occasional heavy slugs of fiber in the feed required use of a vibrating screen loaned especially to this project by Sweco. This commercial unit (4 foot diameter model Sweco screen) provided excellent and fully adequate service throughout the series of demonstrations, and greatly contributed to reduction of operating problems.

Other suspended material in the feed has a strong tendency to foul the membranes, thus resulting in reduced long-term flux rates. Efforts in these studies were made to stay away from expensive pretreatment operations such as reported for waste treatment in other industries in which elaborate pretreatment systems have been employed ahead of

RO processing. Lime and ferric chloride treatment, addition of polyelectrolytes, coagulation, filtration, and air flotation are examples of such advanced pretreatments. In contrast, pretreatment at all demonstration sites in this project study consisted of no more than a 40 to 150-mesh screening with pH and temperature adjustment. However, advantage was taken of the fact that higher degrees of turbulence and mixing at high velocities across the membrane surface in tubular systems help in minimizing concentration polarization and fouling effects.

Initial plans for temperature adjustment were based on reaction rates within the limits of acid hydrolysis above pH 3.0 and of alkaline hydrolysis on cellulose acetate membranes. However, additional criteria were developed on need for maintaining the highest possible operating temperature consistent with obtaining maximum flux rates through the membrane and with maintaining temperatures wherever possible at levels which would help to inhibit microbiological growth and slime formation on the membrane surfaces. Temperature inhibition of microbiological growth can be expected above 40°C, but attempts to operate above 40°C were strictly limited by accelerated chemical hydrolysis reactions on the CA membranes. Later trials have shown nearly all evidence of microbiological fouling ceased when operating temperatures were purposely raised to the 45°C level with the more resistant membranes which have become available after completing design, construction, and operation of the equipment used in these studies from 1968 through mid-1971. Membranes suitable for higher temperature operation are being sought.

FLUX RATE AND REJECTION CHARACTERISTICS DURING MEMBRANE CONCENTRATION PROCESSING

The initial flux rate and rejection characteristics of a membrane with specific cellulose acetate formulation depend upon the thickness of the active layer and the porosity of the membrane as controlled by the solvents used in casting and the degree of heat treatment in the fabrication of the equipment. The flux rate performance of a membrane during concentration processing of any dilute waste is governed by the osmotic pressure and membrane fouling characteristics of the solution. The osmotic pressure of a solution increases significantly with increase in the contents of low molecular weight inorganics. The rate of membrane fouling is low for clean streams, and it becomes severe for solutions containing substantial quantities of finely divided suspended matter in the nature of colloidal suspensoids. Fiber and other larger aggregates of suspended solids are of less concern in tubular systems if they do not accumulate and plug orifices in valves and pumps. The rejection ratio is an important parameter in the design of a reverse osmosis unit for the purpose of concentrating the feed over a wide range or for chemical fractionation systems. For membrane concentration processing, the rejection ratio is defined as the ratio between the concentrations at both sides of the membrane at a certain spot, and it is important here that both of these concentrations should be considered from the standpoint of being measured instantaneously.

Percentage recovery of water and chemicals in a reverse osmosis system having a given membrane area is determined from the overall average values of flux and rejection ratio obtained during the concentration run. The usual concept of these "overall average values" can be misleading since they are generally calculated as the arithmetic average without taking into account the removal of water taking place as the concentration process progresses. In a multistage RO unit designed to concentrate dilute effluents by 10 to 20 times the concentration of the original feed liquor, a large portion of the water is removed in the early stages of concentration, and therefore it is important here to consider the percentage removal of water at various concentration levels in the determination of the overall average values. The overall average value can be mathematically determined as follows:

$$X_{OA} = \frac{\sum_{i} Wi\ Xi}{\sum_{i} Wi} \qquad (6)$$

where

X_{OA} = overall average value of X

Xi = average value of X in the i-th concentration stage

Wi = percent removal of water in the i-th concentration stage

$\sum_{i}$ = summation of all the concentration stages

In the above expression, X can represent a number of important parameters, such as flux rate, rejection ratio, or solids concentration in the permeate. It is important that the calculations should be carried out over a large number of concentration stages in order to determine a true overall average value.

The chemical recovery ratio in a concentrating system represents the amount of dissolved components recovered in the final concentrate. This is of importance in case the concentrate contains valuable chemicals, or if retention of pollution materials in the concentrate is desired. It is calculated as follows:

$$\overline{R} = \frac{F_2C_2}{F_1C_1} = \left(\frac{F_2}{F_1}\right)^{1-R} \qquad (7)$$

where

$\overline{R}$ = chemical recovery ratio

F_1 = feed flow (input)

F_2 = concentrate flow (output)

C_1 = concentration of feed

C_2 = concentration of final concentrate

R = rejection of the membrane

A quick estimation of overall quality of total permeate and its acceptability to meet antipollution quality standards or, alternately, its suitability for reuse can be expressed as follows:

$$\frac{C_p}{C_1} = \frac{(1-\bar{R})}{(1-\frac{F_2}{F_1})} \qquad (8)$$

An example of the kind of information which can be easily obtained from the above equations is presented in Table 23. The calculated data show the final concentrate volume (F_2/F_1); the water to be removed $(F_1 - F_2)/F_2$; the recovery of chemicals by the system $\bar{R}$; and the average concentration of the permeate, C_p obtained at various rejections when concentrating 1 to 10.

TABLE 23

PERFORMANCE OF REVERSE OSMOSIS AT VARIOUS REJECTION RATIOS

R, rejection in percent	99	90	70	50
C_2/C_1 (Concentration Factor)	10	10	10	10
F_2/F_1 (Volume Reduction)	0.10	0.08	0.04	0.01
$(F_1/F_2)/F_2$ (Water Removal)	0.90	0.92	0.96	0.99
$\bar{R}$ (Chemical Recovery)	0.98	0.77	0.38	0.10
C_p/C_1 (Concentration Permeate)	0.02	0.24	0.63	0.90

A number of concentration runs were made using a small-scale unit on various pulping effluents prior to the design of a large-scale trailer unit. The results of these small-scale studies indicated that an overall average flux rate of 7.5 gfd could, at that time, be obtained with the Havens Type 3 membranes then available when concentrating a 1.0 percent solids feed to 10 percent solids concentrate at 25-35°C and 600 psig pressure. The average rejection of solids for these modules were found to be above 90 percent, whereas BOD_5 rejections ranged from 75 to 90 percent. It was also noticed that the membrane rejection of various components did not change significantly with increase in concentrations for most of these pulping effluents.

SYSTEM HYDRAULIC PARAMETERS

The next step in the design of the large-scale trailer unit was to study system hydraulic parameters, mainly velocity and pressure drop. The importance of maintaining higher velocities across the membrane surface to reduce concentration polarization and fouling effects has been emphasized previously. In addition, velocity and pressure drop parameters play an important role in the determination of the best module configuration for a large, multistage concentrating system. Both of these parameters are discussed separately below.

Velocity

In order to overcome the limitations occasioned by reduction in the long-term flux rate and the rejection characteristics of the membrane it is necessary to maintain adequate degrees of turbulence and mixing necessary to minimize concentration polarization and fouling of reverse osmosis membranes.

In the design of a demonstration unit the following assumptions for the minimum velocity were used:

Concentration	gal./min	ft/sec
less than 2 percent solids	1.5	2.5
2 to 6 percent solids	2.0	3.3
6 to 12 percent solids	2.5	4.1

This concept of higher velocities is necessary in keeping the membrane clean and thus maintaining economic levels of long-term, steady flux rates. However, it should be kept in mind that although higher velocities across the membrane can reduce the physical accumulation of solids near the membrane, it cannot alter any chemical or electrical affinity which the solids may have with the membrane. Special problems of pretreatment may arise if such affinities are apparent.

The concept of minimum velocity at various solids levels as concentration proceeds is also an important factor in the determination of the best arrangement of modules. The maximum number of modules which can be put in parallel and the minimum number that have been put in series for each concentration stage is determined on the basis of the minimum velocity required. For given pumping capacities of the pressurizing and booster pumps, the number of modules in parallel decreases proportionally while designing for an increased velocity, while the number in series increases proportionally.

Pressure Drop

The pressure drop in a system depends on a number of factors. First of all, it depends on turbulence and frictional losses related to the velocity in the module. We found for a module of 1968 Havens design having eighteen 1/2-inch tubes, a tube length of 87 inches, and a total membrane area of 17 square feet, that the total hydraulic resistance could be formulated as follows:

$$\Delta P = A\ V^{1.85} \qquad (9)$$

where

ΔP = frictional pressure drop, psi
A = 2.2
V = velocity, ft/sec

In this particular design of module, a substantial percentage of pressure drop was found to take place in the seventeen 180° close return turnarounds.

Pressure drop is one of the important design factors of concern in the selection of the number of modules to be used in series. The loss in volume as concentration proceeds in a series of tubes or modules is also to be considered. The maintaining of a desired minimum level of velocity at any point in the system when connecting a large number of modules in series requires control of the total flow rate going into the system, allowance for the loss in volume, and also consideration of the pressure loss occurring in proportion to the number of modules. Under such conditions, it becomes necessary to add booster pumps to overcome the pressure drop. Therefore, one should optimize the pressure drop against the total flow rate, while selecting the number of modules to be connected in series.

FINAL DESIGN OF THE RO DEMONSTRATION UNIT

The study of various design features as discussed in this report led to establishing specifications for the final design of a large-scale demonstration unit. The specifications were submitted with invitations to bid to ten concerns active in supplying membrane equipment. Two quotations were received. The unit accepted from these bids was designed in detail by the Havens International staff, and built into a 40-foot trailer for mobility, as shown in Fig. 12, 13, 14. All the hardware, except for the modules, was designed for handling up to 100,000 gal./day and a maximum operating pressure of 1000 psig. The original equipment included 396 Calgon-Havens 18-tube modules having 6732 square feet of membrane, plus a reserve of 20 modules. The unit as delivered had a nominal capacity of 50,000 gal./day at an overall average flux rate of 7.5 gfd at 25-35°C and 600 psig pressure. The maximum allowed operating pressure at that time for the Calgon-Havens modules supplied was 600 psig, although the unit was required to pass acceptance tests under full load at 1000 psig. Much credit must be given to the staff of Havens International for the great amount of detailed engineering going into final design and construction of this unit under the pioneering conditions established in the specifications.

Figure 15 provides the flow diagram for the large-scale demonstration unit along with the arrangement of modules in each concentration stage. In order to concentrate 50,000 gallons per day of dilute feed from

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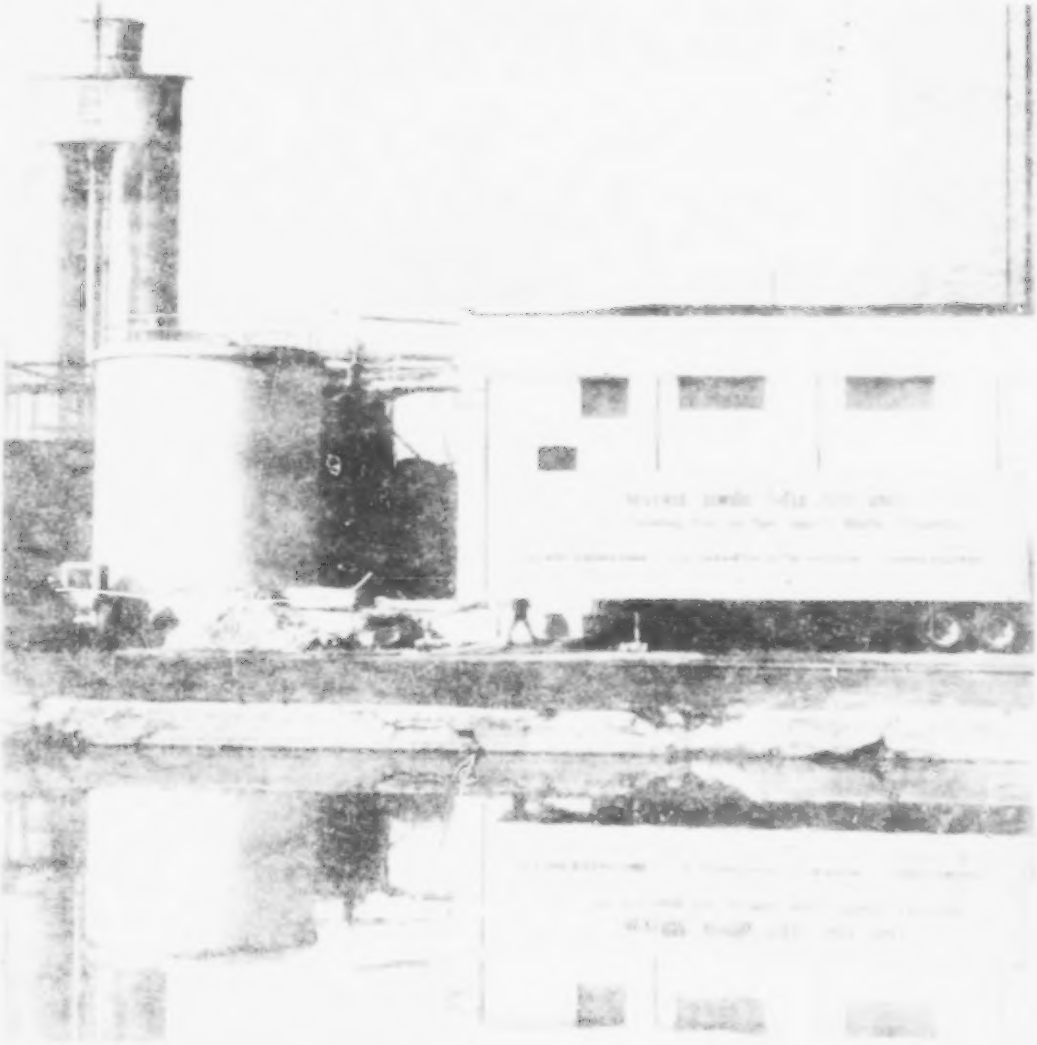

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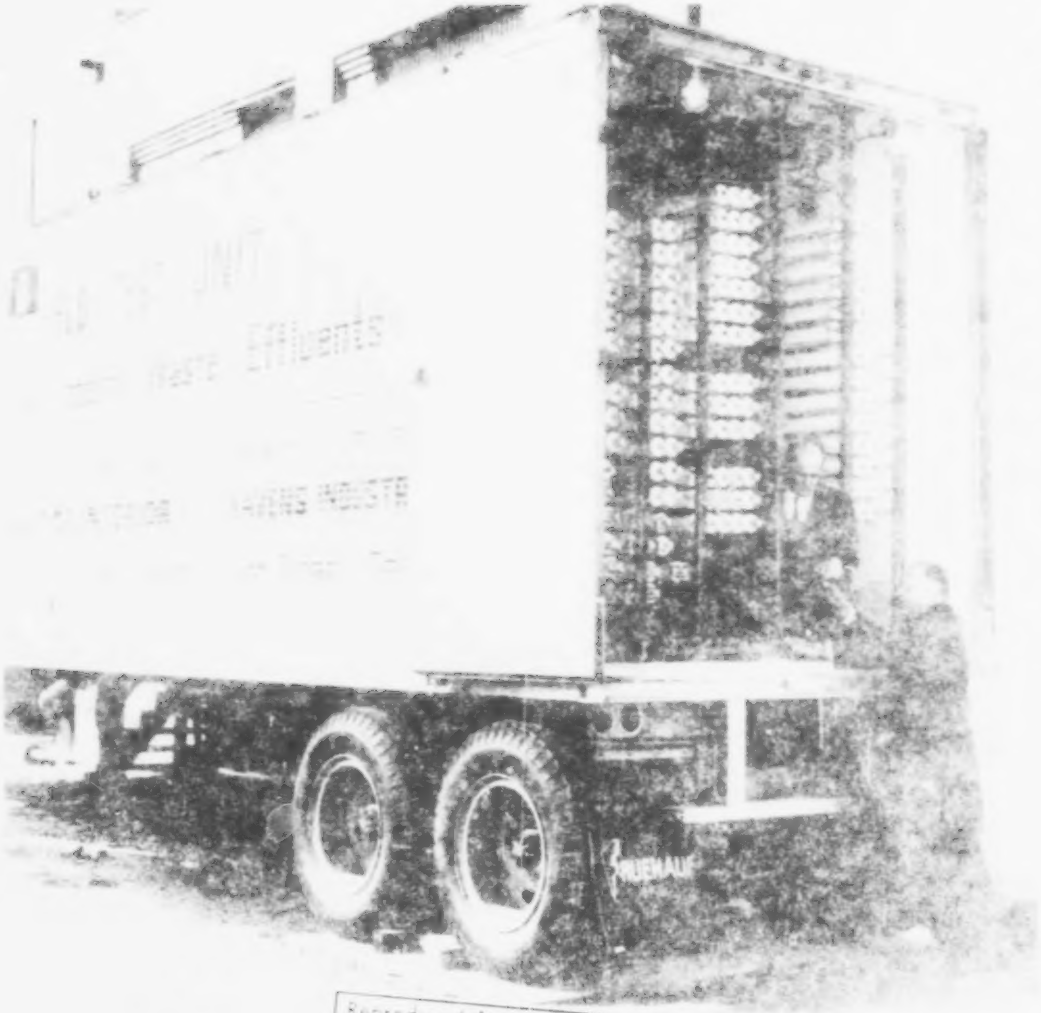
UNIT
Waste Effluents
SAVINGS INDUSTR
FRUEHAUF

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Figure 13. Photograph of RO Trailer. Banks of Tubular Modules Shown as Mounted in Rear Half of Trailer. Similar Banks and [illegible] Access Doors Mounted in Front Half. Access to Control Panel, [illegible] Pumps and Valving Through Center Side Door.

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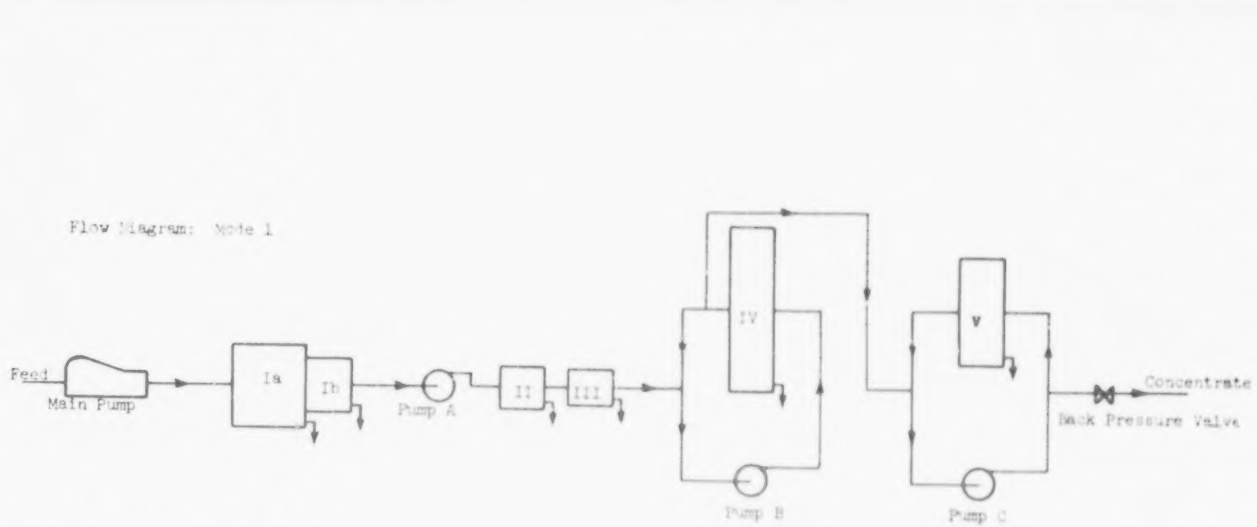
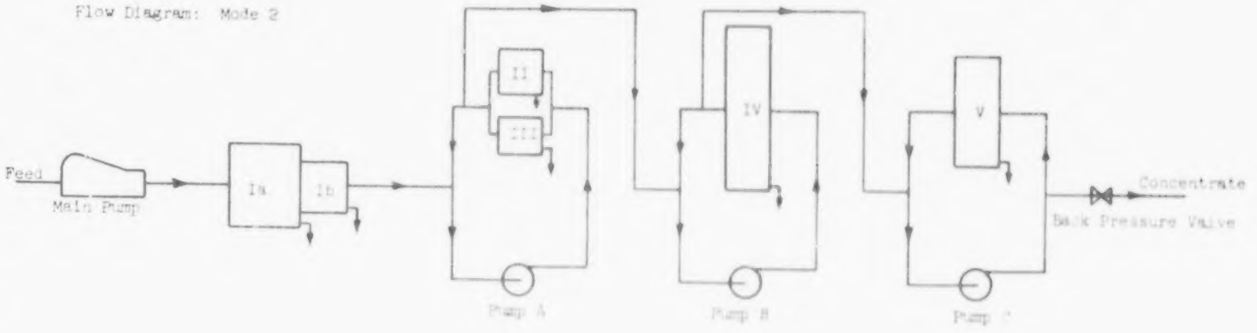
[illegible] instrumentation
[illegible] and visual
[illegible]
[illegible]
[illegible]

Flow Diagram: Mode 1


Feed
Main Pump
Ia
Ib
Pump A
II
III
IV
Pump B
V
Pump C
Concentrate
Back Pressure Valve

Flow Diagram: Mode 2


Feed
Main Pump
Ia
Ib
II
III
Pump A
IV
Pump B
V
Pump C
Concentrate
Back Pressure Valve

	Main Pump:		Pump A:		Pump B:	Pump C:
Max. Capacity	70 gpm		50 gpm		100 gpm	50 gpm
Operating P	1000 psig		720 psig		720 psig	720 psig
ΔP	1000 psig		50 psig		50 psig	100 psig
Bank	Ia	Ib	II	III	IV	V
Modules Parallel	12	12	12	[illegible]	48	21
Series	[illegible]	[illegible]	[illegible]	1	3	3
Total	[illegible]	[illegible]	[illegible]	[illegible]	144	63

15. Flow Diagram of the Large-Scale Reverse Osmosis Unit

1.0 to 10.0 percent solids under straight-through operations, it was necessary to put quite a number of modules in series. Only a small number of modules could be put in parallel due to need for maintaining velocity with limited pumping flow rates. Under the setup of Fig. 13, namely, 20 modules in series in 5 concentrating stages, a large pressure drop of 1200 psig at 3-5 ft/sec was anticipated. This problem could have been solved by adding twelve 100-psig booster pumps. But this, of course, was impractical and not economical, and therefore the system was designed which could be operated with a minimum of two or three recycle loops. Thus, a total of five concentrating stages were installed and the pressure drop at no point in any stage was more than 300 psig below the maximum operating pressure. In the case of high feed intakes (at high flux rates), Banks II and III could be operated without recycle (Mode 1) to satisfy minimum flow requirements. Otherwise, II and III could be operated on a recycle basis (Mode [illegible]).

The main pump was a triplex reciprocating Manton-Gaulin pump driven by a direct current motor with electronic speed control to provide flows in the range of 17 to 70 gal./min at pressures up to 1000 psig. A pressure accumulator was provided to reduce pulsation variations in the system to not greater than plus or minus 0.5 percent of the average system pressure. The recycle pumps were Durco high pressure centrifugal process pumps. The booster pumps [illegible] installation originally employed packed sealing glands for the [illegible] were used in systems with a maximum operating pressure of 300 psig. After careful study of operating conditions undertaken by Durco engineers, these pumps were later replaced by new pumps with mechanical seals especially designed to operate at 1000 psig. The pumps were equipped with John Crane packing single balanced mechanical seals placed in combination with two flushing systems, one at each side of the seals. All metal components in contact with the process solution were 316 stainless steel.

The unit was equipped with a pH meter and controls (Leeds Universal Interlock). The unit was also equipped with safety switches for automatic shut down when pH, temperature, or pressure exceeded set limits. Thus, there was only a minimal need for supervision approximating one man day per day during normal operation and sampling of the system. After delivery and startup tests were completed, the trailer unit was equipped with a "soft" system for pressure pulsing operation. This was designed to accomplish the periodic cleaning of the membrane surfaces in accordance with the principles developed in the preliminary studies. The soft "pulsing" was found to be advantageous in minimizing the membrane fouling caused by colloidal and fine particulate suspended solids of the liquor stream, especially at lower fluid velocities.

SECTION VII

FIVE FIELD DEMONSTRATIONS

FIELD DEMONSTRATION NO. 1

Concentration Processing of Calcium-Base Acid Sulfite Wash Waters

This first field demonstration of reverse osmosis as a concentrating system was conducted on dilute Ca-sulfite pulp wash waters at the Appleton Division (Interlake Mill) of Consolidated Papers, Inc. at Appleton, Wisconsin. The demonstration with the trailer mounted semicommercial unit followed a substantial laboratory and pilot scale testing program (Section V). Additional studies for engineering design and optimization of large installations were conducted later (see Section VIII). The basic data described in Sections V, VI, VII, and VIII are evaluated in Section X for developing the apparent economic picture on use of RO in its present stage of development as a method for concentration processing of dilute effluents of the pulp and paper industry.

Pulping Operations and Methods of Collecting the Wash Water Used in This Demonstration

The Interlake mill pulps Canadian sprucewood by the calcium-base acid sulfite process which was developed more than 100 years ago. The site on the Lower Fox River in Appleton was first used for a small paper mill built in 1853. The present sulfite pulp mill was built in 1891 and the digester system was rebuilt in 1929. This is exclusively a pulping operation and no paper is made. The Mitscherlich horizontal digesters produce a high-grade, long fiber, market pulp which is subsequently fully bleached, for use at other mills in the manufacture of finer grades of business and writing papers and of glassine papers. Many of the older pulp mills in the U.S.A. and Canada employing this Ca-base, batch-type cook are considered to be outdated, have trended toward becoming noncompetitive against newer continuous methods of pulping wood, and have been or are being phased out of business. The difficult-to-solve pollution problems of this acid sulfite pulping process has accelerated the demise of these older mills.

However, there are exceptions to this trend, and continuing efforts under way by the Consolidated staff at this mill, and also in similar research, engineering and commercial studies at a substantial number of other acid sulfite mills, have been directed to modification and installation of improvements to the basic process for the combined objectives of improving the economic competitiveness and to eliminate the pollution problems of acid sulfite pulping. This pulping process still can be considered to have substantial advantages in producing a premium grade, easily bleached pulp, and additionally it produces high yields and modest dollar values of marketable lignin and carbohydrates from the other half of the pulpwood, a fraction which is normally burned for low value heat recovery in the newer pulping processes. However, the economics of complete treatment of all process effluents for pollution control at this mill remains a formidable problem.

A large bibliography[9] with more than 8,600 references, records a century of progress (and of many disappointing failures) deriving from a continuing industry program of chemical research, engineering development, and commercial application of modifications and improvements to solve the pollution problems deriving from these acid sulfite process effluents. No one method of solving all of these problems has been applicable, but much has been accomplished.

Figure 16 presents a flow sheet based upon the overall Ca-base acid sulfite pulping process for producing marketable pulp and spent liquor products, and also shows the various effluents from this process which relate to the serious environmental problems in maintaining operation of acid sulfite mills. These effluents include barking and wood preparation wash waters, dilute pulp wash waters, evaporator condensates, wood fines, pitch and ray cell effluents from fractionators, and also bleach plant effluents. Installation of the evaporation plant at the Interlake mill in 1953 permitted highly effective processing of all of the strong digester liquors that could feasibly be collected and led to production of molasseslike concentrates and spray-dried lignin liquor products which are marketed as dispersants, binders, adhesives, and the like. About 70-75 percent of the dissolved spent liquor solids deriving from the wood cook in the digester can be feasibly collected and processed in this existing system. Development of an economically feasible route for processing the remaining 25-30 percent of the spent digester liquor solids contained in the dilute wash waters has been the subject for much study by the mill staff, and this trial of the reverse osmosis membrane concentration system was designed to establish its possibilities as another alternative route to that end.

A second more detailed flow sheet (Fig. 17) shows the flow within the pulp washing areas of the Interlake mill in the successive steps of draining the strong digester liquor and washing of the pulp prior to final refining in the bleach plant.

All strong digester liquors and early stage wash waters are drawn from the No. 1 liquor tank for concentration by evaporation and spray drying.

The dilute wash waters of concern to this demonstration derive from the fifth stage of washing the digester stock in a batchwise countercurrent washing system. The first four washes are collected and returned for use in the next washing cycle and eventually go to the evaporators. The remaining fifth wash is referred to as "cooling water" by the mill staff. It was found necessary for this demonstration to run some of the fifth wash to the mill sewer because of its high temperature and in order to avoid need for installation of an expensive heat

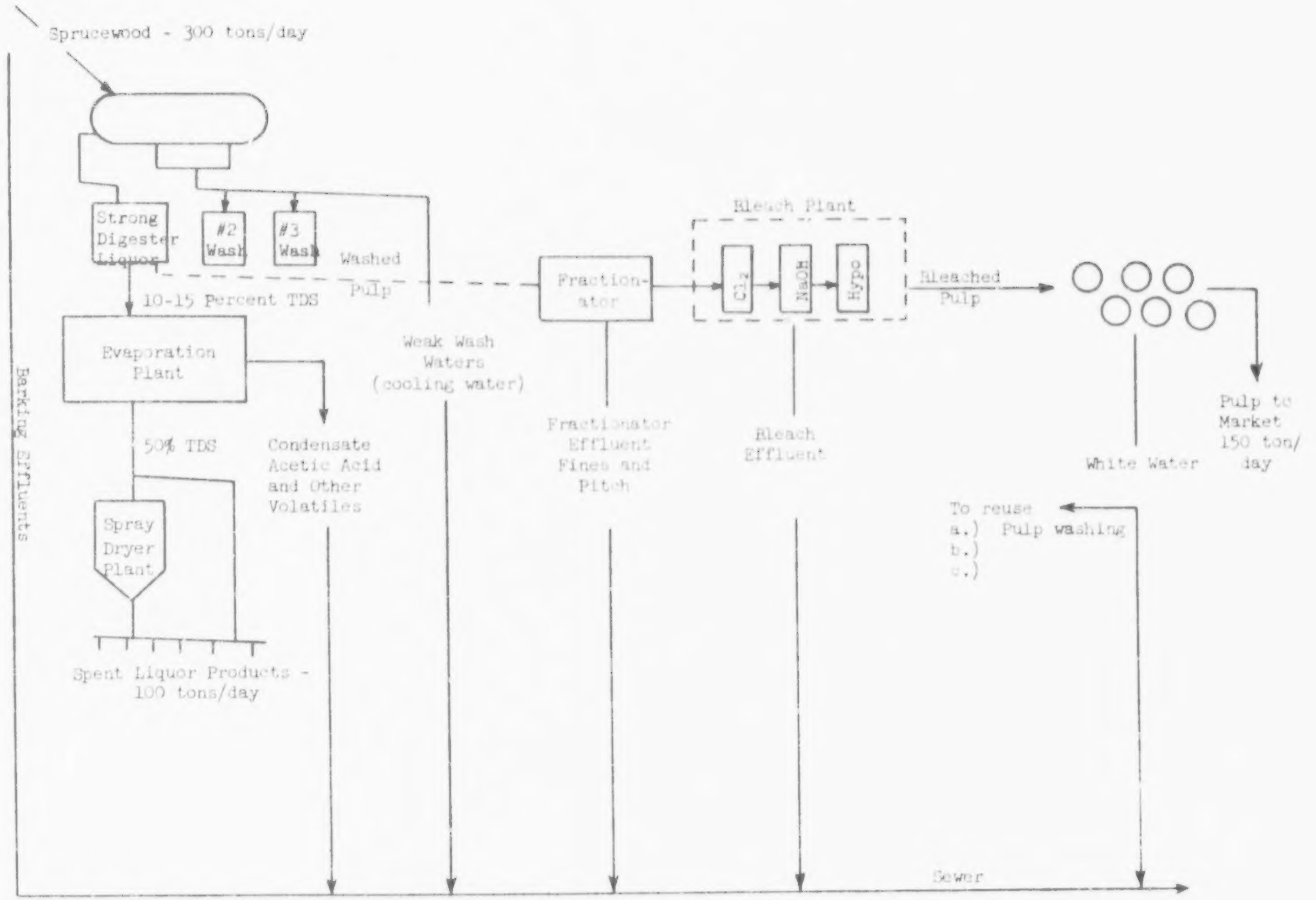
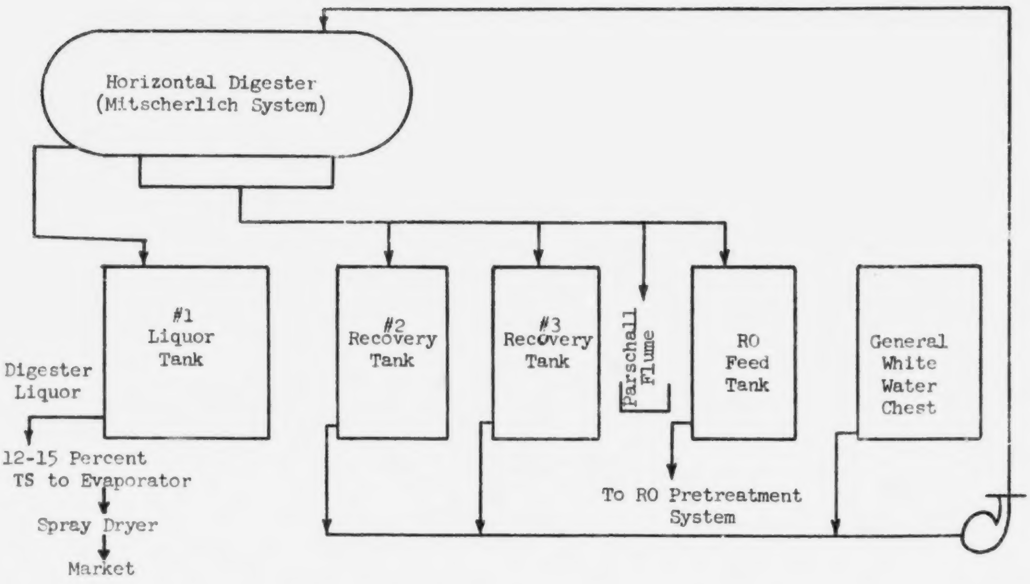

Sprucewood - 300 tons/day
Strong Digester Liquor
#2 Wash
#3 Wash
Washed Pulp
10-15 Percent TDS
Evaporation Plant
50% TDS
Spray Dryer Plant
Spent Liquor Products - 100 tons/day
Condensate Acetic Acid and Other Volatiles
Weak Wash Waters (cooling water)
Fractionator
Fractionator Effluent Fines and Pitch
Bleach Plant
Cl_2
NaOH
Hypo
Bleach Effluent
Bleached Pulp
White Water
Pulp to Market 150 ton/day
To reuse
a.) Pulp washing
b.)
c.)
Barking Effluents
Sewer

Figure 16. Flow Sheet for Calcium-Base Acid Sulfite Pulp Mill


Horizontal Digester
(Mitscherlich System)
#1 Liquor Tank
#2 Recovery Tank
#3 Recovery Tank
Parshall Flume
RO Feed Tank
General White Water Chest
Digester Liquor
12-15 Percent TS to Evaporator
Spray Dryer
Market
To RO Pretreatment System

Washing Procedure:

(A) Blow strong digester liquor to No. 1 liquor tank
(B) 1st Wash with water from No. 2 recovery tank. Drain to No. 1 weak liquor tank (8500 gal./cook)
(C) 2nd Wash with water from No. 3 recovery tank. Drain to No. 1 recovery tank (8500 gal.)
(D) 3rd Wash with water from general white water chest. Drain to No. 2 recovery tank (8500 gal./cook)
(E) 4th Wash with water from general white water chest. Drain to No. 3 recovery tank (8500 gal./cook)
(F) 5th Wash with water from general white water chest. Drain to Parshall flume until temperature less than 95°F, then to RO feed tank. Total (12,000 gal./cook)

Figure 17. Flow Sheet — Washing Cycle and Liquor Collection Calcium-Base Acid Sulfite Pulping. Volumes Given per 14 Ton Cook (10-12 Cooks/Day)

exchange system to bring the temperature down to less than 40°C as needed for these brief trial runs. The remaining flow of dilute wash waters contained an average total solids concentration of about 1.1 percent, and was well suited as a feed stream for the purpose of demonstrating the capabilities of this reverse osmosis membrane equipment for concentrating by a factor of 10 times to give concentrations at 10 percent total solids which could be more economically processed and to provide the minimum volumes which would fit the limited capacity of the existing evaporation plant in any commercial application to be made at this mill.

Full-scale commercial design would advantageously include all of the fifth wash waters, but pretreatment for reducing the temperature might be required. Need for expensive heat exchange equipment might be reduced or eliminated by auxiliary pretreatment steps such as flashing off of the acid volatiles in a combined cooling and SO_2 recovery system. This step to reduce the volatile acid content could also eliminate need for pH adjustment. Additionally, membranes capable of operating at higher temperatures and lower pH levels have become available in 1971 as substantial and important advances over the temperature and pH sensitive reverse osmosis equipment that could be supplied in constructing the trailer-mounted unit for these demonstrations in 1968 through 1970.

DESIGN OF THE EXPERIMENTAL PROGRAM

Laboratory Phases

Section V described the extensive program of preliminary studies upon which these small pilot and large field demonstration trials were based. However, continuing small-scale studies in the laboratory were needed to develop answers to operating problems of pitch fouling, $CaSO_4$ scaling, and the like, as they arose in the field test program. Then, too, equipment suppliers for pumps, valves, membrane modules, and the like, were developing improvements in the course of this program which necessitated the continuance of special tests in addition to the extensive analytical control program conducted in the Appleton laboratory in support of the field trials.

Small Pilot-Scale Field Testing

Operation of the large, trailer-mounted field demonstration unit, designed to process flows ranging from 20,000 to 100,000 gallons per day, was preceded by six months of preliminary study in the mill with a small field unit equipped with 24 modules (7-tube) for processing 1500 gallons per day. The small unit, with about 165 square feet of membrane area, provided important experience in developing performance indices and information on equipment life needed for design of the large-scale runs. However, straight-through operation on dilute feed at 1 percent solids could not sustain reliable and substantial levels of concentration with use of the pumping equipment available and with that limited amount of membrane area. These preliminary studies with the small unit were advantageous in studying the response of the RO system to variables in terms of temperature, pressure, velocity, pH, and especially for preliminary evaluation of fouling problems such as with the pitch contained in these softwood pulping wash waters.

Equipment and Liquor Collection for Small Pilot Runs

Figure 18 shows the schematic diagram for the pretreatment and RO operation. The pulp wash water from the fifth cooling stage was drawn from the digester ahead of the Parshall flume and pumped to a Sweco vibrating screen employing a 125-mesh screen. The screened wash then flowed to the first of two 4000-gallon stainless steel holding tanks. For daily batch-type operation, 50 percent caustic was added manually to adjust the pH to above 3, and the solution was then transferred to the second 4000-gallon storage tank by a centrifugal pump. The second storage tank with a cone bottom permitted settling out of suspended solids. The clarified pulp wash water could then be drawn from the upper levels by a continuously operating centrifugal pump providing feed liquor to the RO unit. A portion of the flow recirculated to the feed line for the second storage tank to avoid freezing during severe cold weather. The feed tank level was controlled by a float valve. A low level float switch, designed to shut down both the Milton Roy high pressure pump and the Hypro recycle pump was also mounted in this feed tank. The main Milton Roy duplex pressurizing pump had 1-1/2 inch diameter plungers operating on an adjustable 3-inch stroke in a Carpenter 20 liquid end equipped with Hastelloy C ball valves which delivered from 0.3 to 6 gallons per minute at pressures to 1135 psig maximum. One-gallon, bladder-type accumulators on each pump served to dampen pressure fluctuations and 0 to 1000 psig bourdon tube pressure gages were installed to measure pressure controlled by 1/2-inch Victor-Acme Type K-20 back pressure regulator valves of bronze construction.

One module bank employed 12 modules with Type 3 membranes, while the second used 6 modules with Type 5 membranes followed by 6 with Type 3. By operating a Hypro pump with a capacity of 3.3 gpm, a feed and bleed recycle system was established, whereby higher concentrations could be obtained.

Summary of Small Pilot Operations

There were three separate phases in the small pilot unit experimental program.

Phase I (1st Through 4th Week) Operation with Old Modules

After a short period of operation with new modules, the presence of pitch in the feed was observed, and also a decline in the flux rate occurred. Operations with the new modules were discontinued and an older group of modules was substituted until it was determined that the presence of pitch did not damage the membranes or irreversibly affect membrane performance. The new modules were reinstalled after it became clear that the flux rate of the fouled modules could be restored to

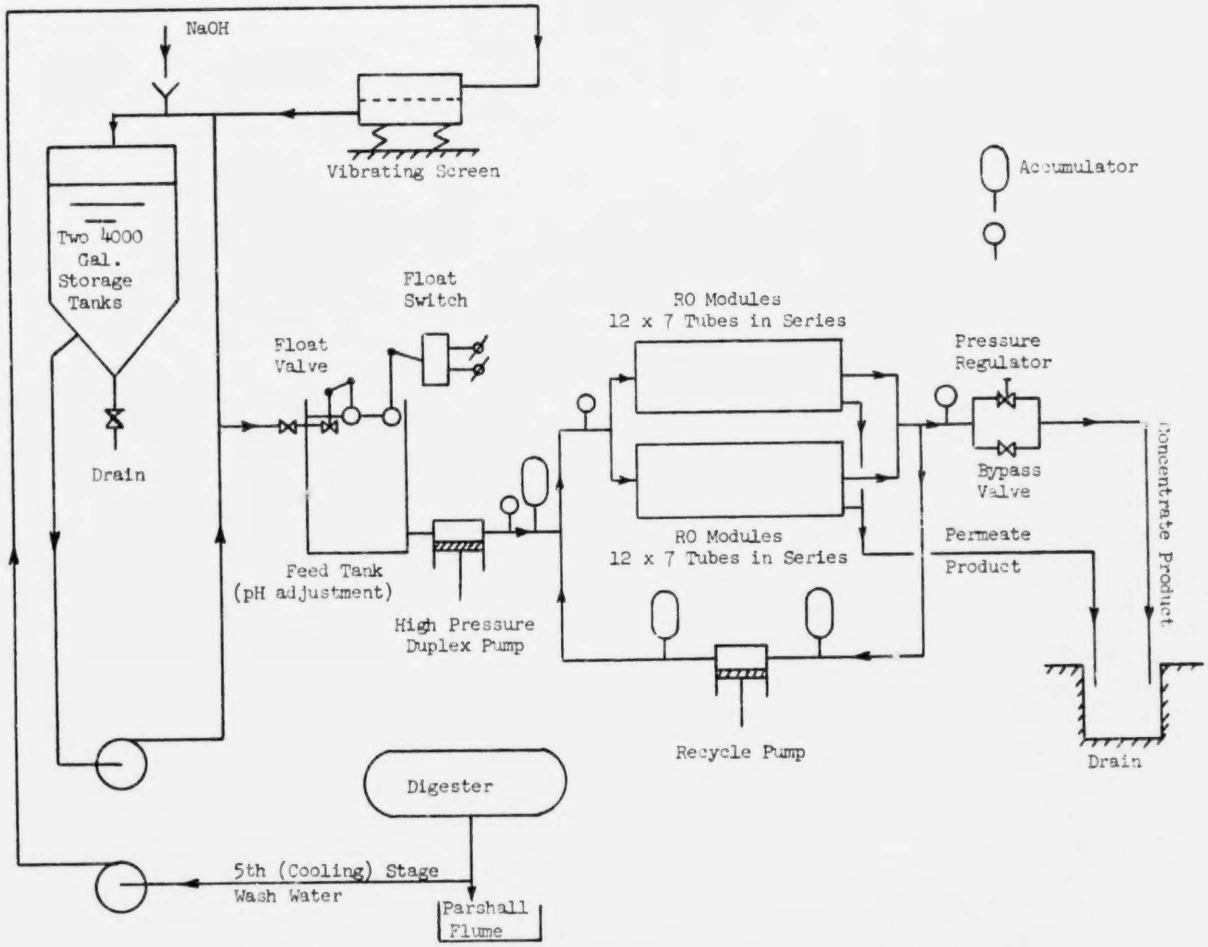

NaOH
Vibrating Screen
Accumulator
Two 4000 Gal. Storage Tanks
Drain
Float Switch
Float Valve
Feed Tank (pH adjustment)
High Pressure Duplex Pump
RO Modules 12 x 7 Tubes in Series
RO Modules 12 x 7 Tubes in Series
Pressure Regulator
Bypass Valve
Permeate Product
Concentrate Product
Recycle Pump
Drain
Digester
5th (Cooling) Stage Wash Water
Parshall Flume

Figure 18. Flow Sheet-Small Pilot RO Unit for Processing Ca-Base Acid Sulfite Pulp Wash Waters

the initial performance by flushing with tap water. Because of the uncertainty of the condition of the older modules, results of this phase are not included in the discussion of data and results.

Phase II (5th Through 19th and 23rd Week)

The new modules, eighteen Type 3 and six Type 5, were put back in operation on a straight-through basis. Velocity, washing frequency, and manually operated pressure pulsing techniques were varied for the purpose of observing and minimizing the fouling of the membranes.

Phase III (20th Through 22nd Week)

The concentrate was recycled to determine system performance at a level of about 5 percent solids concentration.

Data and Results - Small Pilot Operations

Table 24 shows the flux rates of the dilute feed, which ranged from 11 to 19 g/l solids during the run, could be maintained at 9.8 gfd flux and 5.8 gfd flux at 600 psig and 35°C for the Type 3 and Type 5 membranes, respectively. These average flux rates were maintained with an inlet velocity of approximately 2 ft/sec (outlet 1.5 ft/sec), and with pressure pulse of 4-5 minutes duration twice a day. These pulses, effected by manually shutting down the main pressurizing pump, were conducted at 8 am. and 4 pm each day. During the 16 hours between pulses, the flux rate dropped to as low as 6 gfd for the Type 3 membrane, while the Type 5 exhibited much less fluctuation with a normal minimum of 5 gfd. Reference to engineering design and optimization studies described in Section VIII would seem to indicate that concentration polarization could account for only a 10 percent drop in flux after 100 hours of operation, and the remaining loss in flux apparently was due to fouling of the membrane surface. The pulsing and washing studies showed that this reduced permeation effect could be washed away by normal osmotic "back flow" during a pressure pulse or by water flush of the membrane surfaces. Table 24 also provides a summary of weekly average flux rates. Figure 19 gives the detailed flux rate history for Phases II and III of this small pilot run.

Rejection Ratios

Average rejection ratios as determined by composite sampling from each of the 16 weeks of operation on a straight-through basis and for the 3 weeks on a recycle basis are summarized in Table 25. More detailed data are provided in Table 26.

Rejection ratios were excellent in all categories for the tight No. 5 membranes, and still very good for the higher flux No. 3 membranes. Solids, color as measured by optical density, COD and Ca were all rejected at levels of 94.5 percent or higher; BOD_5 at 89-97 percent; and those components (electrolytes) contributing to electrical conductivity

TABLE 24

FLUX RATE SUMMARY
SMALL PILOT RUN ON Ca-BASE ACID SULFITE WASH WATER

	Operating Hours, end of the week	Feed Concn., g/l solids	Flux Rate, gfd	
			Type 3	Type 5
5th Week	426	12.8	10.4	7.0
6	489	12.03	10.8	6.0
7	592	11.05	7.7	5.6
8	644	12.72	10.0	6.3
9	670	11.75	8.8	6.2
10	766	18.43	8.5	5.8
11	870	16.3	6.6	5.3
12	964	13.5	8.1	5.6
13	1060	13.2	9.3	5.7
Average 5-13th week		13.5	8.7	5.9
14	1150	11.5	8.8	5.9
15	1259	12.2	9.9	5.8
16	1349	14.7	9.1	5.9
17	1416	16.3	10.6	5.9
18	1515	11.7	9.7	5.4
19	1617	12.5	9.4	5.1
23	1904	18.9	10.6	6.4
Average 14-19 and 23 week		14.0	9.8	5.8
20	1718	47.3	9.1	4.7
21	1813	54.7	7.5	5.1
22	1833	51.0	6.8	5.0

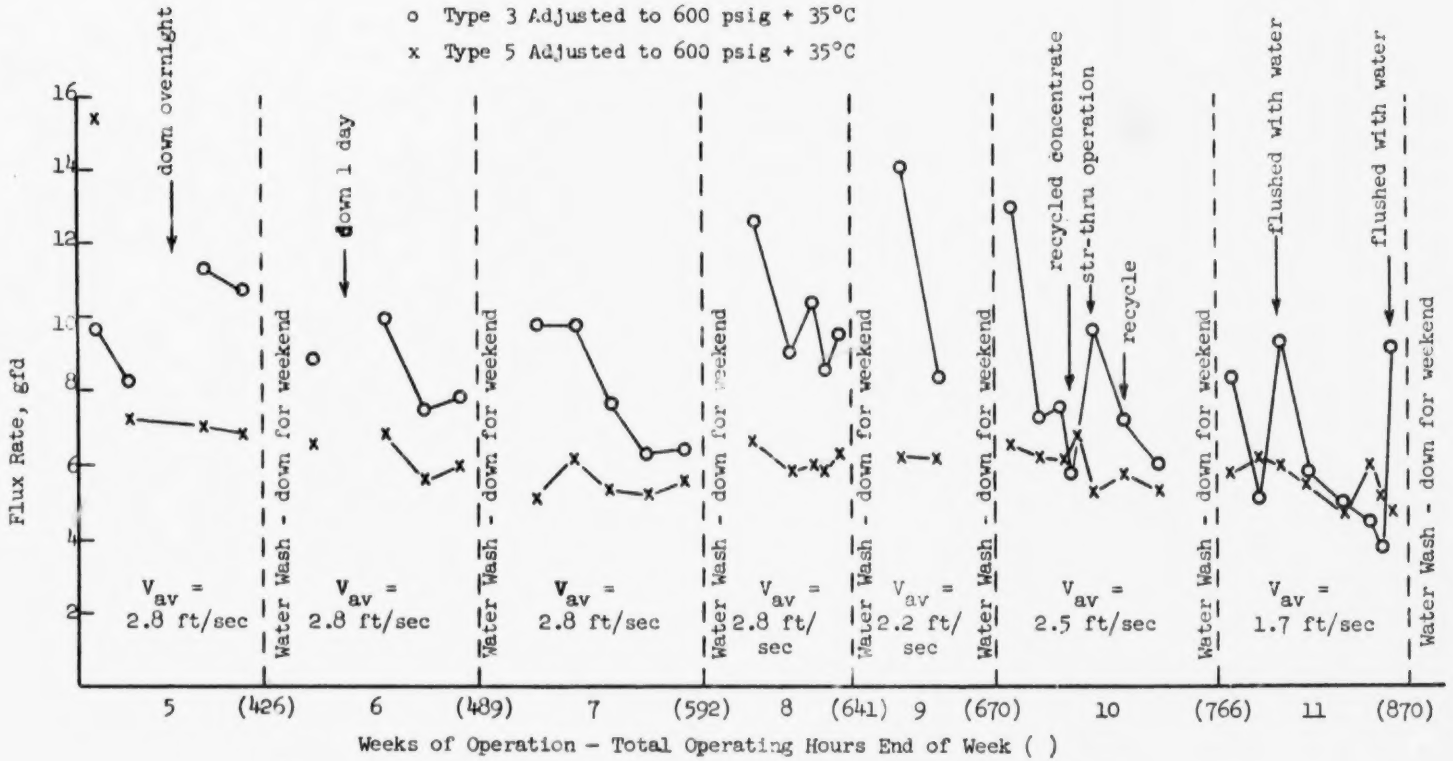


Figure 19. Small Pilot Flux Rate History Ca-Base Acid Sulfite Wash Waters

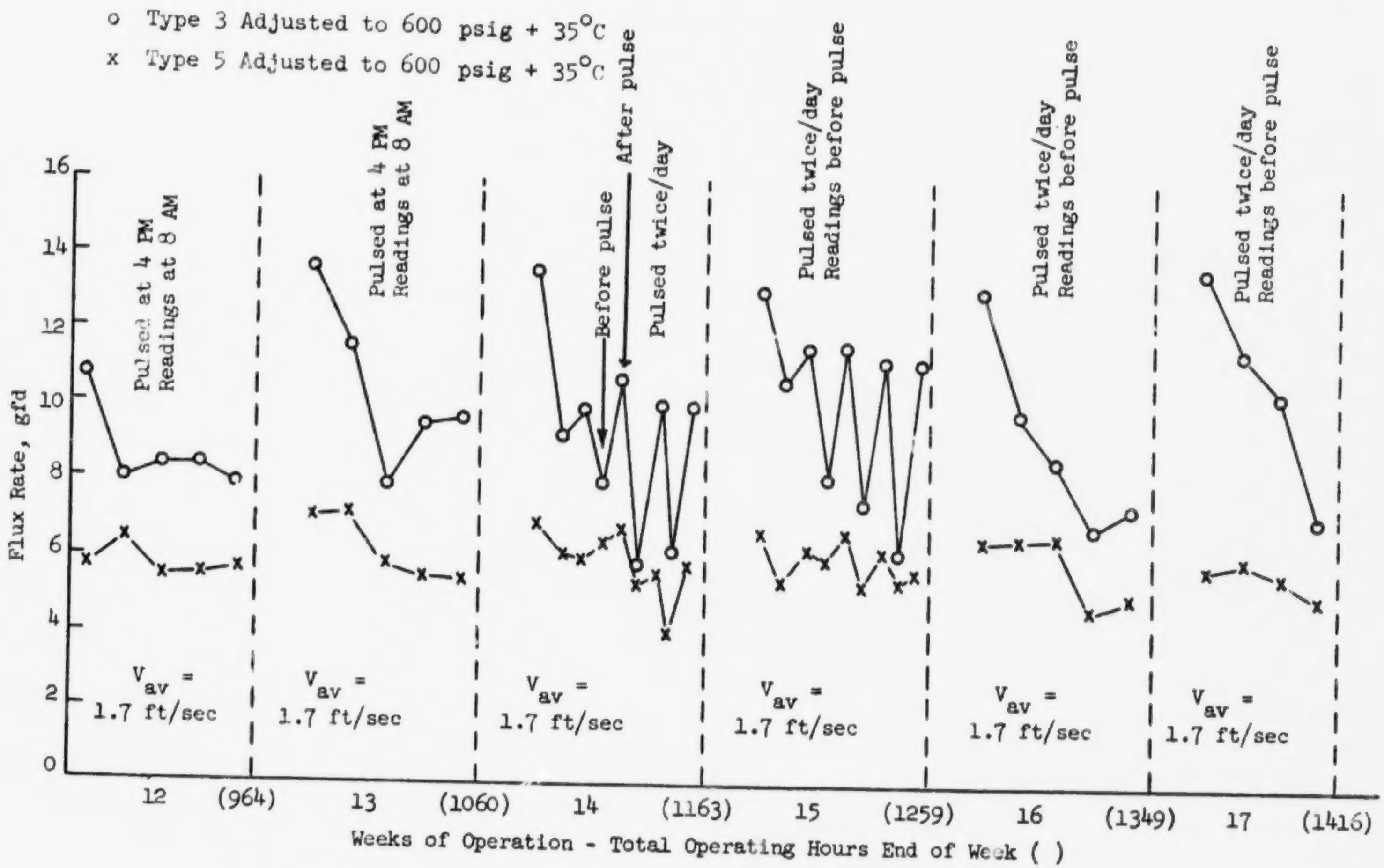


Figure 19 (Continued). Small Pilot Flux Rate History
Ca-base Acid Sulfite Wash Waters
with Small Pilot unit

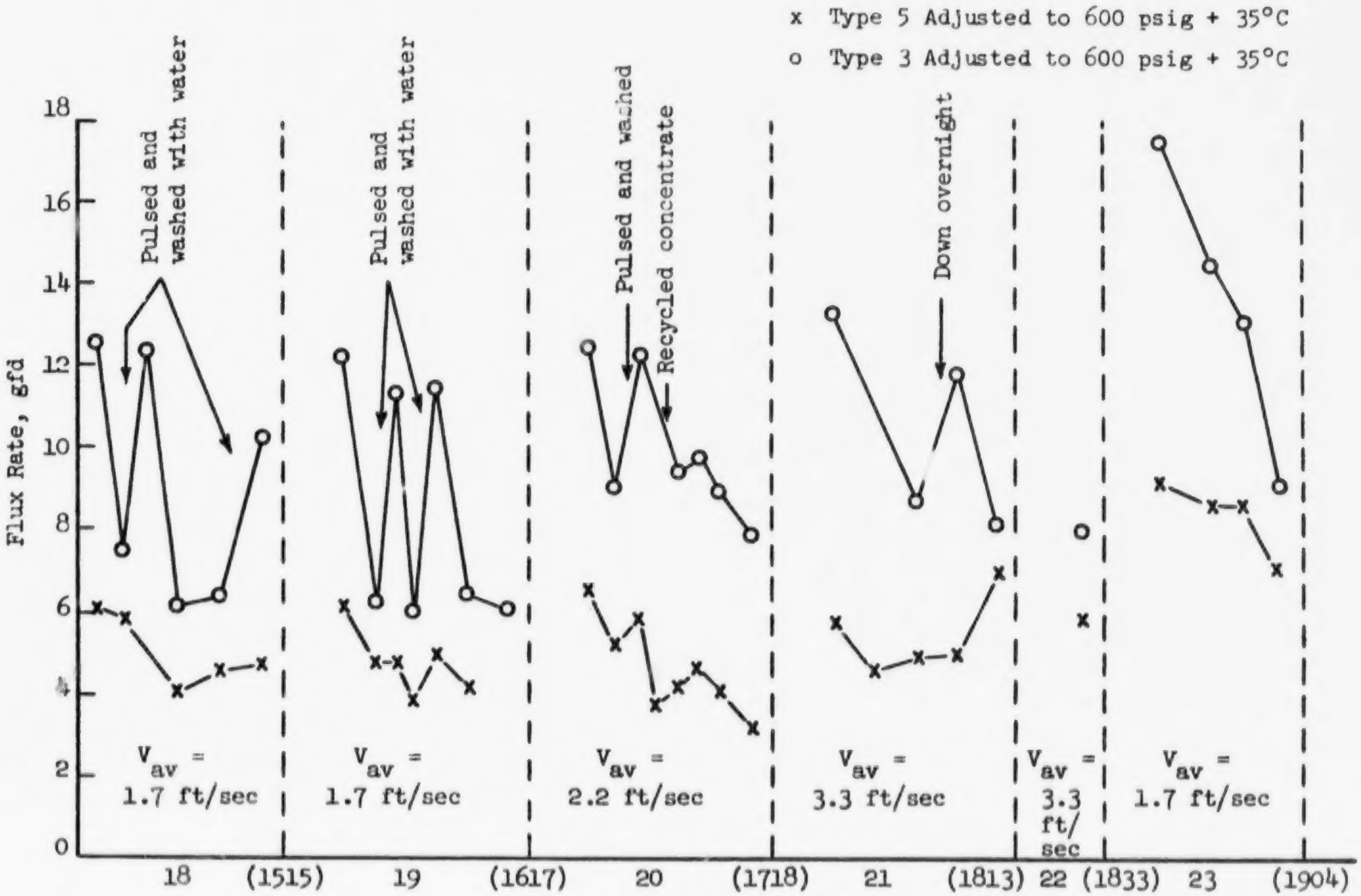


Figure 19 (Continued). Small Pilot Flux Rate History
Ca-Base Acid Sulfite Wash Water

TABLE 25

AVERAGE REJECTION RATIOS - SMALL PILOT RUN
Ca-BASE ACID SULFITE WASH WATERS

	Rejection Ratios, percent			
	Straight-Through Feed 11-19 g/l TS		Recycle Feed Approx. 50 g/l TS	
	Type 3 Av.	Type 5 Av.	Type 3 Range	Type 5 Range
Solids	86	95	90-94	98-9
OD	97	99	99	99
BOD	74	89	77-86	91-97
COD	88	94.5	90-94	98-99
Ca	95.5	98	96-98	99
Conductivity	76	85	72-77	82-91
No. of detn.	(16)	(16)	(3)	(3)

at 85 to 91 percent in the straight-through runs and also in the recycle runs with the No. 5 membrane. Color rejection (OD) remained in the 97-99 percent range for the Type 3 membranes; solids rejection 86 to 94 percent; COD 88-94 percent; Ca 95.5-98 percent; while BOD_5 dropped to 74-86 percent and conductivity 72-77 percent.

These data were the base upon which decision was made favoring use of Type 3 (Havens) membranes then available as the most practical choice for larger scale studies throughout this Research and Demonstration Grant project. Economic advantages were apparent for the No. 3 membrane in providing higher flux rates coupled with adequate and practical levels of rejection for all important components dissolved in the feed liquors in terms of quality of permeate waters for recycle back to the pulp mill for reuse.

Phase III — Small Pilot Concentrating Run

During a period of three weeks, the unit was operated at a concentration of about 50 g/l solids by means of recycling the concentrate. Average flux rates were 7.5 gfd for the Type 3 and 4.95 gfd for the Type 5 membrane at 600 psig and 35°C.

TABLE 26

ANALYTICAL DATA FOR SMALL PILOT RUN
Ca-BASE ACID SULFITE PULP WASH WATERS

Sample No.		No. of Operating Hours	Solids, g/l	Ca, mg/l	Optical Density, 281 nm	BOD, mg/l	COD, mg/l	pH	Specific Gravity	Specific Resistance, ohm-cm
1	Feed		15.45	640	78	3887	14,590	3.72	1.005	278
	Permeate 3		2.04	30	2	1252	1,990	3.89		1600
	Concentrate			790	101	4628	18,940	3.78	1.006	327
	Rej. percent		87	96	97	68	86			79
2	Feed		13.52	600	72	3778	14,690	2.98	1.004	297
	Permeate 3		2.08	30	2	1102	1,882	3.20		1180
	Concentrate			760	84	4502	17,640	3.08	1.006	248
	Rej. percent		84	95	98	71	89			75
3	Feed		14.61	626	74	5013	16,010	3.15	1.005	263
	Permeate 3		1.84	24	2	1048	1,346	3.16		1100
	Concentrate			648	74	5028	17,360	3.12	1.006	257
	Rej. percent		87	96	97	79	92			76
4	Feed		18.47	798	76	6848	20,120	2.72	1.007	321
	Permeate 3		2.80	42	2.8	1906	3,024	2.80		750
	Concentrate			882	93	7298	22,840	2.75	1.009	211
	Rej. percent		85	95	96	72	85			57
5	Feed	426	12.80	582	78	4015	14,720	3.09	1.004	303
	Permeate 3		1.84	32	2	1170	2,176	3.30		1230
	Permeate 5		1.17	20	2	730	1,368	3.11		1580
	Concentrate			648	86	4315	16,580	3.10	1.005	280
	Rej. Type 3		86	94	97	71	85			75
	Type 5		95	97	97	82	91			81
6	Feed	489	12,033	630	90	4640	17,200	3.25	1.007	293
	Permeate 3		2.70	40	4	1720	2,846	3.40		1050
	Permeate 5		0.654	10	2	347	944	2.95		1650
	Concentrate		14,535							
	Rej. Type 3		84	94	96	63	84			73
	Type 5		95	98	98	92	94			83

TABLE 26 (Continued)

ANALYTICAL DATA FOR SMALL PILOT RUN Ca-BASE ACID SULFITE PULP WASH WATERS

Sample No.		No. of Operating Hours	Solids, g/1	Ca, mg/1	Optical Density, 281 nm	BOD, mg/1	COD, mg/1	pH	Specific Gravity	Specific Resistance, ohm-cm
7	Feed	592	11.05	420	64	2870	11,880	3.83	1.003	350
	Permeate 3		1.48	20	2	740	1,460	3.95		1555
	Permeate 5		0.394	10	0.6	240	456	3.49		3610
	Concentrate		12.79	580	73	3573	13,600	3.80	1.004	309
	Rej. Type 3		87	95	97	74	88			77
	Type 5		96	98	99	92	96			90
8	Feed	644	12.72	650	71	2895	10,760	3.20	1.005	278
	Permeate 3		1.94	30	2	1385	1,708	3.28		1055
	Permeate 5		0.60	10	0.9	185	604	2.85		1428
	Concentrate		15.05	770	86	5770	12,980	3.23	1.007	250
	Rej. Type 3		85	95	97	53	84			74
	Type 5		95	98	99	94	94			81
9	Feed	670	11.75	570	71	2822	13,500	4.35	1.005	302
	Permeate 3		1.02	10	1.0	580	1,004	3.98		2290
	Permeate 5		1.07	20	1.0	565	1,075	3.69		1880
	Concentrate		15.8	740	93	3385	17,540	4.80	1.007	236
	Rej. Type 3		91	96	99	79	93			87
	Type 5		93	98	99	80	92			84
10	Feed	766	18.43	880	104	5785	19,800	3.27	1.070	212
	Permeate 3		1.71	30	2	1255	2,080	3.33		912
	Permeate 5		1.19	20	2	760	1,332	3.05		1130
	Concentrate			800	123	5972	22,680	3.37	1.095	188
	Rej. Type 3		91	96	98	78	89			77
	Type 5		94	98	98	87	93			79
11	Feed	870	16.3	770	92	4860	17,920	3.33	1.007	230
	Permeate 3		2.25	30	2	1199	2,125	3.62		860
	Permeate 5		0.60	10	0.81	377	656	3.00		1740
	Concentrate			970	133	5810	23,080	3.45	1.010	187
	Rej. Type 3		86	96	98	75	88			73
	Type 5		96	99	99	92	96			87
12	Feed	964	13.5	710	78	3742	11,800	3.45	1.005	259
	Permeate 3		1.93	30	2	1043	1,785	3.62		1120
	Permeate 5		1.57	10	0.7	424	1,366	3.09		2290
	Concentrate		18.6	930	112	4885	21,240	3.42	1.007	203
	Rej. Type 3		86	96	97	72	84			74
	Type 5		96	99	99	89	88			89

TABLE 26 (Continued)

ANALYTICAL DATA FOR SMALL PILOT RUN
Ca-BASE ACID SULFITE PULP WASH WATERS

Sample No.		No. of Operating Hours	Solids, g/1	Ca, mg/1	Optical Density, 281 nm	BOD, mg/1	COD, mg/1	pH	Specific Gravity	Specific Resistance, ohm-cm
13	Feed	1060	13.2	720	78	4170	14,580	3.50	1.005	
	Permeate 3		2.04	30	2	1333	1,922	3.71		1100
	Permeate 5		1.57	10	0.8	586	622	3.18		2390
	Concentrate		18.3	950	111	5380	19,760	3.46	1.009	
	Rej. Type 3		84	96	97	68	87			76
	Type 5		96	99	99	87	96			89
14	Feed	1163	11.47	590	69.75	3633	12,063	3.90	1.004	326
	Permeate 3		1.37	20	1.54	958	1,349	3.97		1400
	Permeate 5		0.40	10	0.69	328	461	3.48		3910
	Concentrate		15.64	780	96.25	4243	16,545	3.82	1.006	257
	Rej. Type 3		88	96	98	73	89			77
	Type 5		96	98	99	91	96			92
15	Feed	1259	12.19	600	71.2	3418	11,600	3.82	1.006	283
	Permeate 3		1.70	23	1.52	724	1,289	3.80		1110
	Permeate 5		0.47	10	0.58	305	297	3.20		2170
	Concentrate		17.72	810	101.2	4460	16,760	3.72	1.008	220
	Rej. Type 3		86	96	98	79	89			75
	Type 5		96	98	99	91	97			87
16	Feed	1349	14.74	720	85.0	4658	14,920	4.88	1.008	217
	Permeate 3		1.92	23	2.0	1316	1,716	4.08		970
	Permeate 5		0.44	8.5	0.8	416	541	3.38		2930
	Concentrate		21.6	920	117.25	6245	20,980	4.80	1.011	180
	Rej. Type 3		87	97	98	72	88			80
	Type 5		97	99	99	91	96			93
17	Feed	1416	16.26	620	97	5040	16,220	3.57	1.006	242
	Permeate 3		2.27	30	2.20	1352	1,840	3.63		930
	Permeate 5		0.75	15	1.25	510	834	3.15		1640
	Concentrate		22.29	820	134	6633	22,440	3.60	1.009	193
	Rej. Type 3		86	95	98	69	89			74
	Type 5		95	98	99	90	95			85
18	Feed	1515	11.74	440	76.0	3412	12,680	3.60	1.005	303
	Permeate 3		1.69	24	1.64	956	1,466	3.73		1130
	Permeate 5		0.52	8.8	0.61	372	482	3.07		1690
	Concentrate		16.35	694	206.3	4600	17,840	3.57	1.007	244
	Rej. Type 3		86	94	96	72	88			73
	Type 5		96	98	99	89	96			82

TABLE 26 (Continued)

ANALYTICAL DATA FOR SMALL PILOT RUN
Ca-BASE ACID SULFITE PULP WASH WATERS

Sample No.		No. of Operating Hours	Solids, g/l	Ca, mg/l	Optical Density, 281 nm	BOD, mg/l	COD, mg/l	pH	Specific Gravity	Specific Resistance, ohm-cm
19	Feed	1617	12.54	600	78.8	3750	13,340	3.48	1.004	287
	Permeate 3		1.76	30	1.25	1119	1,614	3.62		1180
	Permeate 5		0.57	10	0.33	396	266	3.58		1670
	Concentrate		16.58	740	105.3	4930	17,920	3.45	1.006	233
	Rej. Type 3		86	95	98	73	88			76
	Type 5		95	98	99	90	98			83
20	Feed	1718	--	--	--	--	--	--	--	--
	Permeate 3		0.93	90	5.0	2443	4,365	3.11		700
	Permeate 5		4.73	30	2.15	556	982	2.78		1100
	Concentrate		47.33	2430	423.8	10,800	46,450	2.88	1.019	195
	Rej. Type 3		90	96	99	77	90			72
	Type 5		98	99	99	95	98			82
21	Feed	1813	--	--	--	--	--	--	--	--
	Permeate 3		3.29	37	3.0	2025	4,061	3.55		730
	Permeate 5		0.23	10	0.60	390	602	3.01		1750
	Concentrate		54.69	2480	875	13,600	62,150	3.45	1.025	168
	Rej. Type 3		94	98	99	85	93			77
	Type 5		99	99	99	97	99			91
22	Feed	1833	--	--	--	--	--	--	--	--
	Permeate 3		3.67	28	4.55	1987	2,770	3.47		630
	Permeate 5		0.44	9	0.870	1034	728	2.88		1220
	Concentrate		50.99	1688	367.5	14,150	45,108	3.22	1.024	147
	Rej. Type 3		93	98	99	86	94			77
	Type 5		99	99	99	93	98			89
23	Feed	1904	12.33	529	77.2	3855	14,506	5.17	1.007	323
	Permeate 3		1.52	23	2.20	1152	1,808	4.21		1510
	Permeate 5		0.37	6	1.52	351	470	3.78		5050
	Concentrate		18.87	785	175	5730	22,090	4.68	1.010	260
	Rej. Type 3		88	96	89	73	88			79
	Type 5		97	99	98	91	97			94

An observation of substantial interest to these overall laboratory, pilot, and field studies for concentration and also fractionation processing of a variety of pulp and paper waste waters was especially apparent in these 3 weeks of sustained operation of the small pilot unit at higher levels of solids concentration. The rejections for both the moderately open No. 3 membranes and the tight No. 5 membranes increased 5 to 10 percent as the concentration progressed on a feed and bleed program. This has been observed repeatedly in processing substrates with a range of molecular size in the dissolved solids contained in the original feed material. This increase in rejection observed with concentration of mixed feeds of large and small molecular weight compounds may seem to be counter to the decreased rejection of small molecular weight solutes such as NaCl that is commonly observed at increasing levels of concentration of brackish water and the like.

In the case of these pulp mill effluents, the rejection increases in later stages of the overall concentration as the low molecular weight materials passing the membranes (e.g., sodium chloride, and especially the low molecular weight volatiles such as methyl and ethyl alcohol, acetic acid and sulfur dioxide) are being bled from the system in the first stages of a concentrating system. The remaining higher molecular weight materials such as sugars and lignin continued to be rejected quite well by the tighter RO membranes and the degree of membrane rejection increases as the content of these higher molecular weight dissolved materials increases in the feed to the succeeding stages of concentration. The significance of these fractionation effects will be discussed elsewhere in reviewing the several demonstrations on various wastes studied in this overall report.

Large-Scale Field Studies with the Trailer Mounted Demonstration Unit

The extensive laboratory and RO studies of concentrating the spent wash waters from this mill extending back for more than a year coupled with the six-month runs on the small pilot unit as described above provided a firm base of experience on which to design the experimental program for the large trailer unit under construction during the summer and fall months of 1968. The mill staff had substantially completed installation of the liquor collection, the pretreatment, and feed liquor pumping and control system well in advance of delivery of the trailer-mounted demonstration unit. This unit was delivered by the manufacturer October 12, 1968 and was installed and given preliminary running tests over a period of 2-1/2 weeks. The experimental program and collection of data started November 1, 1968.

Equipment for Pretreatment

"Cooling" stage wash water from each digester was collected in an 45,000-gallon tile lined storage tank, mixed with remaining liquor from previous cycles, and pumped to the pretreatment facilities. The storage tank was normally operated nearly full and at the feed rate of 45,000 to 50,000 gallons daily; this provided for an average hold time of 1.5 to 2 days. A recirculating line at the storage tank served to mix the incoming waters. Pretreatment consisted of screening through a 120-mesh screen and pH adjustment. Much of the suspended solids apparently settled out in the bottom of the storage tank since the small basket screen available for use apparently served the purpose without need for cleanout during the 3-month run, although it was found to be coated with pitch when dismantled at the end of the run. The pH was adjusted from the raw feed level of between 2 and 2.5 to between 4 and 4.5 by means of a 50 percent caustic solution with automated pH control. Some difficulty with an old pH control unit during the first weeks forced the installation of a new controller after which reliable performance was achieved. Caustic was added to the first of two mix tanks. The pretreated water was pumped by centrifugal pump to the inlet of the triplex piston pump. Figure 20 shows the flow sheet for pretreatment and RO trailer unit operations at this site. A photograph, Fig. 64 (Appendix A), shows the pretreatment section in operation.

Trailer Operations (Process Conditions)

The main pressurizing pump operated at discharge pressures between 550 and 600 psig to feed pH adjusted and screened dilute feed to Bank Ia which was in series with Ib for the multistage system. Banks II and III were operated in parallel throughout the demonstration, and fed Bank IV and then the final Bank V stage. The configuration of the system is summarized in Table 27. This table also gives the velocities estimated to be required to overcome concentration polarization and fouling as determined by preliminary field trials and laboratory work.

TABLE 27

MODULE BANK CONFIGURATION-TRAILER UNIT
Ca-BASE ACID SULFITE PULP WASH WATERS

	No. of Modules	No. of Parallel Flow Paths	No. of Series Modules	Minimum Velocity
Bank Ia/Ib	90/36	18/12	5/3	2.4 ft/sec (1.5 gpm)
Bank II/III	30/24	10/8	3/3	3.2 ft/sec (2 gpm)
Bank IV	144	48	3	3.2 ft/sec (2 gpm)
Bank V	63	21	3	4.0 ft/sec (2.5 gpm)

A summary of water recoveries and average flux rates is given in Table 28, while a detailed summary of the process conditions and resulting flux rates for those times during which samples were taken is given in Table 29.

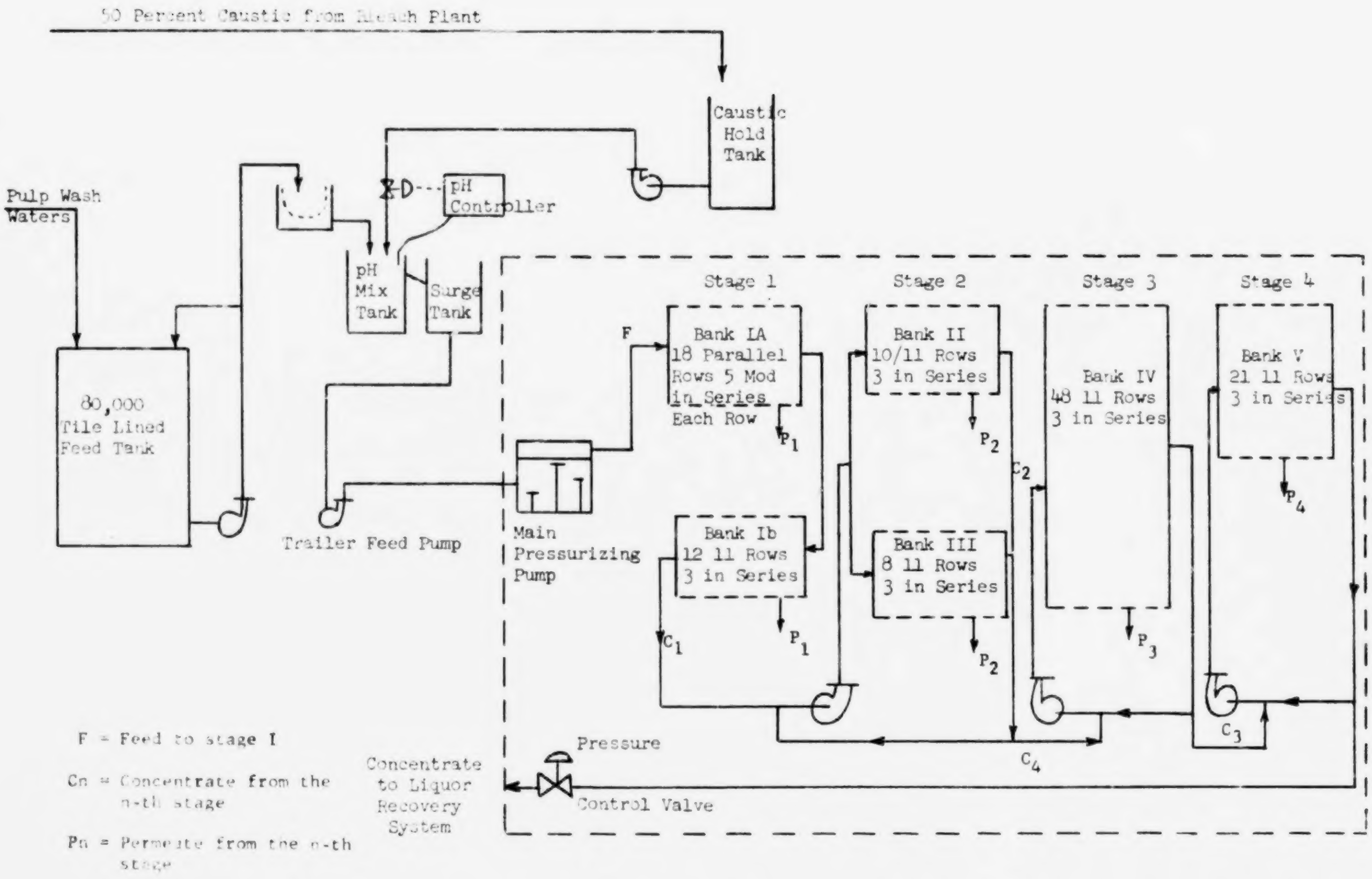

50 Percent Caustic from Bleach Plant
Caustic Hold Tank
Pulp Wash Waters
80,000 Tile Lined Feed Tank
pH Controller
pH Mix Tank
Surge Tank
Trailer Feed Pump
Main Pressurizing Pump
F
Stage 1
Stage 2
Stage 3
Stage 4
Bank IA 18 Parallel Rows 5 Mod in Series Each Row
Bank Ib 12 11 Rows 3 in Series
Bank II 10/11 Rows 3 in Series
Bank III 8 11 Rows 3 in Series
Bank IV 48 11 Rows 3 in Series
Bank V 21 11 Rows 3 in Series
P1
P1
P2
P2
P3
P4
C1
C2
C3
C4
Pressure
Control Valve
Concentrate to Liquor Recovery System
F = Feed to stage I
Cn = Concentrate from the n-th stage
Pn = Permeate from the n-th stage

Figure 20. Flow Sheet-Pretreatment and Trailer Operation Ca-Base Acid Sulfite Pulp Wash Waters

TABLE 28

TRAILER DATA AVERAGES
Ca-BASE ACID SULFITE PULP WASH WATER

Period Operating Hours	Average Intake gal./day	Average Recovery of Product Water	Average Concentration Final Concentrate, solids percent	Average Temperature, ^{o}C.	Average Flux Rate, gfd/day
0-100	46,000	90	12	23	6.9
100-200	39,000	85	9	24	5.2
200-268	35,000	90	12	26	4.8
Removal of $CaSO_4$ in Bank V					
268-400	48,000	83	6	28	6.2
400-500	44,000	80	6	27	5.7
500-587	45,000	78	5.5	28	5.7
Wash-up with Detergent					
587-690	52,000	82	6	28	6.4

TABLE 29

DETAILED SUMMARY OF TRAILER OPERATIONS WHILE PROCESSING Ca-BASE ACID SULFITE PULP WASH WATERS

Sample Set	Operating Hours	Bank I				Bank II/III				Bank IV				Bank V						
		Temp/Av Pressure	Solids, g/l	Flux Rate,[a] gfd	Velocity, ft/sec	Temp/Av Pressure	Solids, g/l	Flux Rate,[a] gfd	Velocity, ft/sec	Temp/Av Pressure	Solids, g/l	Flux Rate,[a] gfd	Velocity, ft/sec	Temp/Av Pressure	Solids, g/l	Flux Rate,[a] gfd	Velocity, ft/sec	Solids	Overall Flux Rate, gfd	No. of Modules
1	57	22/515	10		2.6	22/465	20		2.6	22/452	46		3.1	25/462	99		3.4	99	5.4	387
1a	100	21/525	10		2.1	22/520	14		3.5	22/500	44		3.1	25/492	74		2.3	74	4.0	387
2	125.5	21/535	10		2.4	21/527	12		3.2	21/507	29		3.1	22/505	44		2.5	44	4.6	387
3	155	25/540	12		2.7	25/502	14		3.2	25/490	42		3.1	27/505	71		3.3	71	5.4	387
4	175.5	25/490	14		3.0	25/480	14		3.2	26/456	39		3.1	27/435	59		3.0	59	.9	387
5	203	24/517	12		2.1	24/512	15		3.3	25/500	46		3.1	27/500	80		3.0	80	[illegible]	387
6	223	27/537	14		2.4	27/537	16		3.3	27/527	60		3.1	29/522	100		2.3	100	6.4	324
7	289	30/505	13.5		2.4	30/485	16		3.7	30/482	62		3.1		– Out of Service –			62	5.3	324
	325	29/525	13.5		2.4	29/502	16		3.8	29/465	52		3.2		– Out of Service –			52	5.0	324
9	336.5	24/512	12	3.23 (4.94)	2.8	24/465	14	6.25 (10.95)	4.1	23/387	29	11.5 (28.5)	3.1	23/455	51	9.65 (18.46)	3.5	51	5.1	387
10	379	27/475	15	4.88 (7.80)	3.2	27/405	16	6.18 (12.55)	3.9	26/400	35	8.8 (19.5)	3.1	27/435	58	10.25 (20.36)	3.9	58	6.0	387
11	435	29/490	13	4.73 (7.05)	2.9	28/435	15	6.83 (12.18)	4.2	28/422	29	6.7 (13.5)	3.1	28/455	53	11.25 (20.02)	3.9	53	5.3	387
12	485	29/490	14	3.40 (5.06)	2.8	29/507	15	3.42 (4.82)	4.0	29/505	42	6.34 (9.25)	3.1	31/548	78	4.42 (5.52)	3.9	78	6.1	387
13	520	32/500	11	4.44 (6.04)	2.9	32/405	14	4.22 (7.75)	4.2	31/440	29	7.22 (12.28)	3.1	31/460	52	8.64 (14.18)	3.9	52	5.2	381
14	563.5	25/510	11	3.55 (5.32)	2.8	24/498	13	3.43 (4.96)	4.1	24/492	24	5.9 (9.55)	3.1	24/515	45	7.44 (11.30)	3.8	45	5.3	381
15	619.5	33/487	14	6.52 (9.00)	3.0	33/427	17	6.07 (10.13)	4.3	32/418	36	6.95) (12.7)	3.1	32/445	62	7.84 (13.65)	3.9	62	5.3	381
16	645	28/530	14	5.48 (7.44)	2.8	28/517	16	5.28 (7.39)	4.2	29/517	46	5.98 (8.44)	3.1	32/540	133	5.02 (6.67)	3.9	133	6.3	381
17	666	24/520	14	4.00 (5.96)	2.8	24/455	15	2.64 (4.33)	4.2	23/487	25	5.37 (9.04)	3.1	25/520	31	2.82 (4.34)	3.9	31	4.6	381

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[a] ( ) Adjusted to av. pressure of 600 psig and 35°C.

After about 100 hours of operation, the appearance of calcium sulfate precipitate in the concentrate in Bank V began to affect the performance of this bank. After the unit had operated for 268 hours, the problem became severe as evidenced by a total flow rate which had dropped substantially from the normal 40 gpm. The pressure drop increased from 70 to 120 psi. The permeate rotameters for individual banks had not yet been installed, but there were indications the flux rate in that bank had dropped off. Up until this time, Bank V had been operated to achieve concentrations as high as 16 percent total solids. Calcium salts were observed to be precipitating at that level of total solids. Laboratory tests on the cleaning of $CaSO_4$ were indicated as previously described in Section V. Cleaning by EDTA solution was found to restore the modules in Bank V to the original conditions.

Polyphosphate Experiments

The concentration of dilute pulp wash waters from the 1 percent solids level to 6 or 7 percent solids is a substantial achievement in itself, but substantially less than the 10-12 percent desired for evaporator feed. Since the membrane system seemed capable in all other respects of achieving concentration in the 10 to 16 percent solids range, it was decided to try to inhibit precipitate formation by the addition of polyphosphates.

Three laboratory experiments were conducted. In the first, a solution of Orlene M, an organic heat-resistant polyphosphate, was added to Bank V to a concentration of 50 mg/l, with Bank V total solids at 9.5 percent. No precipitate was noticed in the system. However, a considerable drop in flux rate from 7.5 gfd to 3.5 gfd was attributed to film formation in the membrane by excess polyphosphate.

The experiment was repeated with 20 mg/l polyphosphate at a total solids of 8.5 percent. This was apparently satisfactory in that no precipitate or drop in flux rate was observed. However, the experiment was prematurely terminated by mechanical problems.

The third experiment at 20 mg/l polyphosphate and a total solids of 12.5 percent again exhibited the scaling due to calcium sulfate.

Time did not permit further experiments during this field trial to pinpoint the conditions necessary to obtain a final concentrate of 10 percent or greater. However, it is apparent that precipitate formation and scaling can be inhibited and that scale already formed can be removed from the membrane surface. Earlier experience in laboratory and pilot studies indicating feasibility of concentrating to 10-12 percent solids was confirmed by later experience which indicated that optimization of hydraulic system design with higher velocities would permit concentrating the liquor to 10 percent solids or higher without need for chemical additives.

Since 80 percent of the water or better is removed in Bank I, II/III, and IV at concentrations less than 7 percent, either of the above methods applied to the 20 percent of remaining feed volume might be practiced in a commercial system at reasonable incremental cost.

Fouling of Membrane Surfaces

After the first few days of operation at high flux rates, indications of low flux rate in Banks I and II/III were observed. After the installation of permeate rotameters to monitor the flow rates of each of the banks individually, the reduced flux rates in these banks became readily apparent. The flux rate of Bank I had dropped to 4.9 gfd while Bank II/III was 11 gfd. Further washing tests were conducted on a laboratory scale (see Section V).

Clean-up with a 300 mg/l solution of Polytergent B-300, at a recirculation rate of 1 to 1.5 gpm/module (1.6-2.4 ft/sec) partially restored the flux rates to 10.0 gfd at 600 psig and 35°C for Bank I and 12.7 gfd at 600 psig and 35°C for Bank II/III. This clean-up did not restore the flux rate to the extent shown possible in laboratory tests. The following weekend the modules were cleaned with the same solution at recirculation rates between 2 and 2.5 gpm/module (3.2-4 ft/sec). This clean-up followed after the last operations on liquor feed at this demonstration site were concluded, and prevented recheck of the flux rate with the wash water feed. However, a check with tap water showed the following flux rates when adjusted to 600 psig and 35°C:

Bank V to Bank I	20.9 gfd
Bank II/III	23.9 gfd
Bank IV	20.0 gfd
Bank V	21.4 gfd

This indicated the flux rates were well restored and the trailer unit was moved to Green Bay for the second field demonstration on NSSC white water as described in the following subsection.

Flux Rates

The results of the Appleton field demonstration run in terms of actual flux rate determinations are compared with calculated values at standard conditions of operating at 600 psig and 35°C in Table 29. These data were for the period after the occurrence of calcium sulfate precipitate in Bank V and the pitch and silicate problems in Bank I and II/III. Calculated values are obtained from the measured permeation rate and specific gravity of the liquor for each bank by determining the solids from Fig. 21 and the osmotic pressure from the osmotic pressure curve for Ca-base acid sulfite liquor (Fig. 50 of Section VIII). A temperature correction of 2.1 percent/°C was applied, and the rate of driving force at 600 psig to the driving force at the given operating pressure (neglecting the osmotic pressure of the permeate) was used to convert the readings to 600 psig and 35°C. The accuracy is dependent upon the

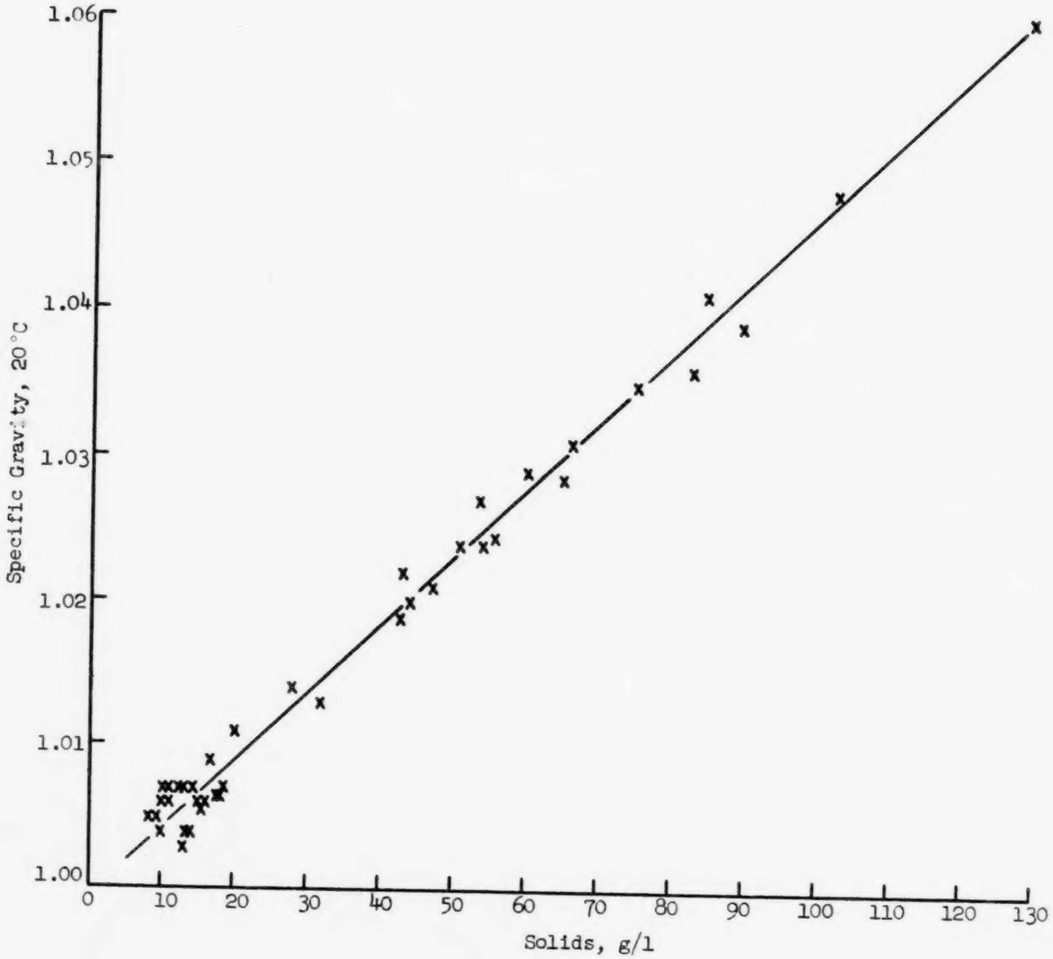

Figure 21. Solids Concentration vs Specific Gravity Field Run on Ca-Base Wash Waters

operating conditions but for those readings at pressures of about 500 and temperatures of 25-30°C, accuracy should be within 10 percent. This may deteriorate to 20 percent for those readings more distant from the reference point.

Recoveries and Rejections

Table 30 summarizes the recovery data for the run with the large trailer unit, while Table 31 gives the complete summary of analytical data. The calculated rejection values would not be indicative of module performance over a wide concentration range if the rejections varied significantly. In this case, however, performance at different concentrations by individual banks does not vary significantly, and thus, those data correlated at the average concentration do give representative data. The recoveries are calculated from the rejections and water recovery $\overline{R} = (F_2/F_1)^{1-R}$ (7).

Pretreatment by Neutralization with NaOH for pH Adjustment

Adjustment of the feed liquor pH to a level in the range of 3.5 to 4.0 was specified by the membrane equipment supplier as necessary to avoid acid hydrolysis and damage to the cellulose acetate membranes in these field trials. The cooking liquors have a pH of about 2.0 to 2.5 after discharging from the digester, principally due to the content of free and loosely combined sulfur dioxide. This sulfur dioxide is routinely steam stripped in commercial practice such as in yeast plants and an analogous stripping effect occurs in commercial evaporation of the liquors. In both cases, the pH rises to a level in the range of 3.5 to 4.0. Steam stripping could not feasibly be installed for these brief small-scale, field trials but chemical neutralization was easily substituted by use of approximately 0.5 g. NaOH per liter (4.3 lb/1000 gal.) throughout these trials with the small pilot and with the large field demonstration unit.

Adjustment of the pH to 7.0 was tried during one brief period of operation to determine the possible increase in BOD_5 rejection that might be achieved. This resulted in formation of a precipitate and a reduced flux rate, but no significant change in BOD_5 rejection was observed (Sample 17, Table 31).

Energy Consumption

Power usage was calculated on the basis of the several conditions of a 50,000 gpd input for the feed concentrations available at this mill, an inlet pressure of 600 psig, 90 percent efficiency for the motor and main high pressure pump, and a 40 percent efficiency for the centrifugal pumps. Under these operating conditions energy consumption was found to be 4.8 Kwh/1000 gal. of feed liquor for pressurizing the system with the main pump and an additional 6.4 Kwh/1000 gal. for the booster-recycle operations. This amounted to a total of 11.2 Kwh/1000 gal. or 562 Kwh/day.

TABLE 30

RECOVERY DATA FOR TRAILER UNIT WHILE PROCESSING Ca-BASE ACID SULFITE WASH WATERS

Sample No.	Water Recovery, percent	Recovery, percent				
		Solids	BOD_5	COD	Ca	OD
1	90	95	85	94	98	99
2	75	97	89	95	99	99
3	85	98	87	95	99	99
4	82	95	87	94	97	99
5	87	96	87	95	98	99
6	90	96	85	94	98	99
7	75	93	84	91	99	99
8	70	95	86	94	99	99
9	75	92	81	92	97	99
10	75	93	85	93	97	98
11	75	89	74	88	98	98
12	75	89	70	80	96	99
13	73	92	81	93	98	98
14	75	87	85	93	98	99
15	75	91	93	93	98	98
16	90	87	69	87	96	96
17	66	89	83	91	95	95
Range	66-90	87-98	69-89	87-95	95-99	95-99

During the last two weeks when the average intake was about 50,000 gpd, we found an actual average power consumption of 640 Kwh/24 hours. This also includes power for instrumentation, lights, and the centrifugal pump ahead of the main pressurizing pump. Although the power consumption by the electric space heater was also measured by the same Kwh meter, it was not included in the last figure, due to the fact that the warm liquor in the modules and manifolds heated the trailer automatically to a temperature well above the preset temperature on the thermostat, so the heater was not activated during RO operations. All in all, both power consumption figures seem to be in good agreement.

TABLE 31

ANALYTICAL DATA FOR TRAILER UNIT WHILE PROCESSING
Ca-BASE ACID SULFITE PULP WASH WATERS

	Sample Set	Neutralized Solids, g/l	Calcium mg/l	OD at 281 nm	BOD_5, mg/l	COD, mg/l	CoPt Units	pH	SpGr
Feed	No. 1	8.05	430	48.7	2970	8960	350	5.00	1.005
Permeate		1.03	20	1.6	924	1306	<5	4.61	
Concentrate		84.30	5040					4.60	1.041
Rejection, percent		97.8	99.3	99.5	93.6	97.4			
Feed	No. 2	8.02	440	45.9	2870	9140	230	4.87	1.005
Permeate		0.58	10	0.80	589	838	<5	4.40	
Concentrate		42.89	1480					4.20	1.022
Rej., percent		97.8	99.0	99.2	89.4	95.6			
Feed	No. 3	9.40	530	51.5	3355	11,120	230	3.83	1.005
Permeate		0.82	20	1.76	841	1119	<5	3.69	
Concentrate		74.89	4280					3.72	1.035
Rej., percent		98.9	99.2	99.2	93.1	97.6			
Feed	No. 4	10.21	510	57.7	3705	11,930	270	3.92	1.006
Permeate		0.86	20	1.11	811	1293	<5	3.88	
Concentrate		60.00	1650					3.92	1.029
Rej., percent		97.55	98.15	99.4	92.8	96.6			
Feed	No. 5	9.85	530	57.6	3755	11,540	270	3.87	1.007
Permeate		0.85	16	1.10	901	1260	<5	3.63	
Concentrate		79.49	4300					3.35	1.039
Rej., percent		98.1	99.3	99.6	93.5	97.4			
Feed	No. 6	11.14	570	66.2	4090	13,308	320	3.91	1.007
Permeate		1.16	19	1.43	1153	1689	<5	3.95	
Concentrate		102.56	4500					3.35	1.048
Rej., percent		98.0	99.3	99.6	92.9	97.2			
Feed	No. 7	13.04	630	78.4	4445	14,300	350	3.88	1.007
Permeate I		1.14	11	1.06	814	1148	<5	3.83	
Perm. II/III		1.22	12	1.25	839	1227	<5	3.90	
Perm. IV		1.87	15	1.80	1079	1846	<5	3.68	
Perm. Total		1.67	14	1.66	1074	1663	<5	3.62	
Conc. I		16.52	760					3.24	1.009
Conc. II/III		19.69	1090					3.26	1.011
Conc. IV		66.32	3720					3.51	1.031
Rej. I		92.3	98.4						
Rej. II/III		93.3	98.7						
Rej. IV		95.7	99.2						
Feed	No. 8	12.58	620	70.2	4270	13,540	350	4.1	1.007
Permeate		1.31	10	1.50	927	1391	<5	4.1	
Concentrate		53.63	1850					4.2	1.027
Rej., percent		96.0	99.2	98.9	87.7	94.6			
Feed	No. 9	11.09	600	60.20	3440	11,580	250	3.90	1.006
Permeate		1.86	30	1.46	1123	1742	<5	3.25	
Concentrate		50.80	2560					3.75	1.024
Rej., percent		93.9	98.1	99.1	84.5	93.7			

TABLE 31 (Continued)

	Sample Set	Neutralized Solids, g/l	Calcium mg/l	OD at 281 nm	BOD$_5$, mg/l	COD, mg/l	CoPt Units	ph	SpGr
Feed	No. 10	13.99	680	74.40	4870	16,430	300	4.52	1.007
Permeate		1.99	30	2.78	1324	1956	<5	4.02	
Concentrate		59.50	2720	355.2				5.30	1.029
Rejection, percent		94.6	98.2	98.7	87.6	94.9			
Feed	No. 11	13.57	670	67.20	4220	14,400	220	4.05	1.004
Perm. I		1.40	10	1.32	1068	1282	<5	3.85	
Perm. II/III		1.37	10	1.49	1086	1298	<5	3.95	
Perm. IV		1.56	10	1.63	892	1416	<5	3.91	
Perm. V		4.00	80	4.55	2280	3850	<5	4.02	
Perm. Total		2.10	30	2.07	1292	2020	<5	4.02	
Conc. I		15.97	760					4.12	1.0055
Conc. II/III		17.59	820					4.15	1.0065
Conc. IV		31.64	1390					4.25	1.013
Conc. V		55.39	2650					4.28	1.0245
Rej. I		90.5	98.6	98.2	75.9	91.6			
Rej. II/III		91.8	98.7	98.1	77.2	92.2			
Rej. IV		93.7	99.1	98.5	86.0	93.8			
Rej. V		90.8	96.0	97.7	74.2	89.6			
Feed	No. 12	13.25	686	70.0	4220	14,050	300	3.75	1.003
Permeate I		1.29	12	1.09	761	1118	<5	3.58	
Perm. II/III		1.40	17	1.66	818	1252	<5	3.55	
Perm. IV		1.78	16	1.54	992	1540	<5	3.68	
Perm. V		7.18	243	18.80	3585	7670	<5	3.78	
Perm. Total		2.65	45	5.41	1440	2562	<5	3.30	
Conc. I		15.4	746					4.05	1.006
Conc. II/III		17.95	854					4.30	1.0065
Conc. IV		42.76	1740					4.25	1.019
Conc. V		82.56	4260					4.05	1.036
Rej. I		91.0	98.3	98.5	82.6	92.4			
Rej. II/III		91.6	97.9	98.0	82.9	92.3			
Rej. IV		97.1	98.8	98.8	82.2	93.8			
Rej. V		88.5	91.9	99.3	57.1	80.8			
Feed	No. 13	13.57	650	68.0	4210	15,620	350	4.32	1.003
Permeate		2.0	27	2.10	1221	1632	<5	3.68	
Concentrate		55.23	2450					4.52	1.024
Rej., percent		94.2	98.3	98.7	85.4	95.4			
Feed	No. 14	10.43	490	58.0	3185	11,560	250	4.32	1.004
Permeate		1.36	19	1.29	802	1380	<5	3.82	
Concentrate		17.93	1900					4.45	1.020
Rej., percent		90.4	98.4	99.1	88.0	94.7			
Feed	No. 15	15.1	690	80.6	5325	16,750	400	4.18	1.004
Permeate		2.29	27	2.85	594	2232	<5	3.90	
Concentrate		65.0	3260					4.38	1.0285
Rej., percent		93.5	98.6	98.7	95.8	95.4			

TABLE 31 (Continued)

	Sample Set	Neutralized Solids, g/l	Calcium mg/l	OD at 281 nm	BOD_5, mg/l	COD, mg/l	CoPt Units	pH	SpGr
Feed	No. 16	11.9	580	62.0	3650	12,280	300	4.15	1.003
Perm. I		0.95	9	1.32	588	862	<5	4.08	
Perm. II/III		1.00	10	1.68	600	1026	7	4.15	
Perm. IV		1.68	14	2.40	1038	1449	<5	4.07	
Perm. V		5.44	86	7.75	3425	5278	10	4.14	
Perm. Total		1.80	22	2.80	1188	1775	<5	4.25	
Conc. I		16.3	780					4.50	1.006
Conc. II/III		18.7	880					4.50	1.007
Conc. IV		47.2	2490					4.60	1.021
Conc. V		133.5	5660					4.65	1.060
Rej. I		93.3	98.7	98.2	86.0	94.0			
Rej. II/III		94.3	98.8	98.1	88.0	94.0			
Rej. IV		94.9	99.2	98.6	88.2	95.6			
Rej. V		94.0	97.6	98.0	72.1	91.3			
Feed	No. 17	10.0	250	62.0	3185	10,860	300	6.18	1.004
Permeate		1.37	19	5.05	822	1610	25	5.66	
Concentrate		29.2	720					5.55	1.014
Rej., percent		90.6	96.1	95.6	84.8	91.8			

Trailer Operations — Mechanical Performance

During this first demonstration, start-up problems associated with the development of a new unit operations process hindered the gathering of process data. Most of the problems were with associated equipment, especially the mechanical seals on the centrifugal booster pumps and for the pH equipment, and not with the modules themselves. The modules performed well mechanically in these first months of their overall service life. Eight modules out of 387 had to be replaced during the 690 actual operating hours at the demonstration site. Six had to be replaced due to fiberglass support tube rupture, one due to failure of tube seals (inserts), and the eighth was replaced because it was so badly plugged with calcium sulfate that the scale could not be removed without damaging the membrane. This was then tabulated as a mechanical failure. One failure occurred in Bank I, one in Bank II/III, two in Bank IV, and three in Bank V. Based on eight replacements in 690 hours, the unit averaged about 86 hours between module failures in this first three month trial. The manifolding system on the trailer was designed with cut-out valves for each five modules, and this permitted maintaining the unit in operation without need for shutdown to replace individual modules.

Operating Hours — Downtime

The schedule called for operation from early Monday morning until late Friday afternoon each week, or about 100 hours per week. Thus, during the 15 weeks of the demonstration, 1386 hours were available and the unit was actually in operation for 690 hours, resulting in an operating efficiency of 46 percent. However, during the last two weeks after the startup mechanical problems were taken care of, an operating efficiency of 100 percent was achieved. Prime causes of downtime are listed in Table 32. Individual mechanical problems resulting in downtime are discussed in the following paragraphs.

The pH controller initially used for the liquor pretreatment system in the mill was an old model purchased in 1945 and for which repair parts were difficult to obtain. A new pH meter, controller, and transducer were purchased by The Institute of Paper Chemistry, for temporary use on this project, and after its installation, no further problems were encountered. The pH meter control system installed on the trailer worked well and provided automatic shutdown to protect the membrane system when the feed pH control system failed in the mill.

Initially, the three centrifugal pumps, used as recycle pumps, were supplied with a type of packing gland which did not seal reliably at the system pressures of 400-600 psig. These glands were replaced with mechanical seals having a flush system. This arrangement proved satisfactory for Pumps A and B, circulating liquor at concentrations below 7 percent, but at higher concentration with the attendant calcium sulfate precipitate, the spring in Pump C became clogged with calcium sulfate. It operated well when the final concentration was reduced to 7 percent solids for the final run.

The $CaSO_4$ scaling problem was described earlier in the report and resulted in system outage while the Bank V modules were being cleaned.

Equipment to accomplish pressure pulsing as described in Section V was installed on the trailer during this first run. Design criteria were needed as based on actual operation prior to fabricating the pressure pulsing system. Several days were required for installation and testing but were not charged to the downtime summary.

DISCUSSION OF THE DATA FOR DEMONSTRATION NO. 1

During the 690 hours of actual operation, the semicommercial demonstration unit treated about 1,200,000 gallons of dilute sulfite wash waters. More than 45 tons of solids were concentrated at recoveries ranging upward of 85 percent in the form of a 6-16 percent solids concentrate, and were sent to existing evaporators for further concentration processing. At the same time, between 80-90 percent of the feed liquor was recovered as a clear and colorless renovated water free of pitch, microbiological growth, and foam problems which might affect reuse in the mill. The high quality of this water for reuse in the mill and the important pollution control capabilities were well demonstrated in this extended run with indicated recovery of 69-89 percent of the BOD_5, 87-95 percent of the COD, 87-98 percent of the total solids, 95-99 percent of the calcium, and an average of 99 percent of the color in the concentrate. The flux rates averaged between 5 and 6.5 gfd for the overall concentration at temperatures between 25 and 35°C, and pressures between 400 and 550 psig, and with final total solids concentrations ranging from 6 to 12 percent.

TABLE 32

CONSOLIDATED (APPLETON DIVISION)
RO TRAILER OPERATION - DOWN TIME

Period		Total Hours		Hours	Hours Lost				Ruptured
From	To	Available	Operating	Lost	Pumps	pH	Scale	Other	Modules[f]
10/31/68	11/25/68	364	102	262	244	--	--	18[a]	0
11/25/68	12/6/68	199	101	98	--	82	--	16[b]	1
12/9/68	12/20/68	198	91	107	78	2	27	--	1
12/23/68	12/30/68	- - - - - - - - - - - - - - Down for Christmas - - - - - - - - - - - -							
12/30/68	1/16/69	180	76	104	9	--	66	29[c]	1
1/20/69	1/31/69	240	126	114	--	32	8	74[d]	2
1/31/69	2/14/69	205	194	11	3	5	--	3[e]	1
Total		1386	690	696	334	121	101	140	6
Percent of available		100	49.8	50.2	24.1	8.7	7.3	10.1	
Percent of down time				100	48.0	17.4	14.5	20.1	

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[a] High pressure cut-off.

[b] High pressure cut-off.

[c] Frozen pipe, power failure, high pressure cut-off.

[d] Installation of pressure pulsing equipment, power failure, oil in effluent guage.

[e] High temperature cut-off.

[f] System not shutdown for module replacement.

The permeate water was remarkably clear, colorless and low in dissolved materials. Complete reuse to replace fresh water at a number of process points within the mill would be desirable. Volumes of this permeate at 40 gpm were insufficient for conducting significant mill tests in the time available, but the mill operating staff were of the opinion this clear, clean water could be recycled without problems of build-up of color, scale, slime, or other undesirable components. Stripping of sulfur dioxide and other volatiles, such as acetic acid, might be desired to obviate any build-up of such materials in some areas of reuse, but this would be of less concern in other recycle streams.

The feed liquor used in these demonstration trials in laboratory, small pilot, and in the large trailer-mounted field unit was available at between 1 and 2 percent total solids, but was otherwise representative of the total pulp mill effluent being discharged to the river in the form of digester cooling and pit waters totaling 1,200,000 gallons daily at about 0.68 percent total solids. The feasibility of RO concentration processing of the total volume of digester cooling and pit water cannot be seriously considered.

The cooling wash water which was subject for study in this demonstration had a total solids content averaging 11.48 g/l and a BOD_5 of 3.87 g/l from 17 weekly assays during the 3 months of operating the field unit at this mill. The exact volume of "cooling" water which might be recovered for RO processing at those concentrations has been difficult to determine because of its mixture with pit waters in a common effluent line from a number of digesters, but separation of these flows would seem to indicate a volume in the range of 400,000 to 700,000 gallons daily, and an assumption of 500,000 gallons may be reasonable for purposes of the following estimations. Recent assays of the total of all mill effluents, of the combined digester cooling and pit waters, and estimates calculated on the basis of 500,000 gallons of cooling water flow provide a base for evaluating the possibilities for substantially reducing the pollution problems by use of RO concentration processing of those mill effluents (Table 33).

From these data it seems possible to consider RO as a means of processing the "cooling" wash water to achieve as much as 1/3 reduction in soluble solids and in BOD_5 as based on the total liquid effluent discharges from all operations of pulping, bleaching and evaporation at this mill. The 50,000 gal./day of RO concentrate produced in a volume reduction by a factor of 10 to 1 could conceivably be processed with nominal expansion of the existing evaporation, spray drying and marketing program for spent liquor solids.

Module maintenance and replacement costs which developed unfavorably in following field demonstrations as discussed in subsequent sections of this report raised serious questions on RO operating charges. This factor substantially affects feasibility for achieving these projected advantages under practical conditions. Disposal problems might be substantially alleviated by sale of the concentrated and spray dry spent liquor products in the long-term and successful program practiced for nearly 20 years at this mill.

TABLE 33

ESTIMATED POLLUTION LOADS FROM VARIOUS EFFLUENT FLOWS

	Total Mill Flow All Effluents	Combined "Cooling" and Pit Waters	Percent of Total Mill Flow	Estimated Values for Digester "Cooling" Water Only	Percent of Total Mill Flow
Volume, gal./day	10,650,000	1,180,000	(11.1)	500,000	(4.5)
Total soluble solids, tons/day	70.35	29.21	(41.5)	24.0	(34.0)
BOD_5, tons/day	23.70	14.16	(60.6)	8.17	(34.5)

In any case, the demonstration provides an alternative to other possible routes under consideration for reducing the substantial losses of pulping liquor solids and importantly reducing the total pollution loading of this mill. State pollution control surveys of November-December, 1970 indicate the total digester pit and cooling waters account for 4.5 percent of the suspended solids, 46 percent of the dissolved solids, 48 percent of the total suspended and dissolved solids, and 59 percent of the BOD_5 in the total of all effluent waters including the fractionator effluents and evaporator condensates. If the fractionator effluents were to be effectively processed in a clarifier installation, the capabilities for reducing the mill environmental problems by RO processing of the digester cooling and pit waters could increase to 18.8 percent reduction for suspended solids, 52 percent reduction for the total of soluble solids and suspended solids, and 68 percent reduction for the total BOD_5 loading from this mill. The evaporator condensates and bleach plant effluents would then become the principal remaining problems for final solution of major water pollution problems at this mill.

The choice of methods which might be used to bring the effluent discharge loadings within acceptable limits becomes a matter of evaluating the economy of the various possible processing routes in terms of capital and operating charges. The economics of RO treatment are discussed separately in Section X.

FIELD DEMONSTRATION NO. 2

Concentration Processing of Neutral Sulfite Semichemical White Water by Reverse Osmosis

This subsection describes field studies with the pilot unit and with the larger trailer-mounted demonstration unit at the neutral sulfite semichemical pulp mill of Green Bay Packaging, Inc., in Green Bay, Wisconsin. Laboratory work which preceded the demonstration is described in Section V, while additional work to obtain engineering design information optimizing a commercial-scale installation for this waste water is described in Section VIII.

A research and demonstration grant to Green Bay Packaging, Inc., from the Environmental Protection Agency has followed the completion of the studies which are the subject for this report and are currently in progress (December, 1971). Full-scale plant design studies are resulting from the new grant and, if the outcome is favorable, could result in the first commercial installation of reverse osmosis in the pulp and paper industry.

Pulping, Paper Machine Operations, and Wash Water Collection

This integrated pulp and paperboard mill produces 210 tons of unbleached fiber daily by the neutral sulfite semichemical process employing batch digesters. About 200,000 pounds of spent liquor dissolved solids are produced. Approximately 70 percent of the solids are contained in the digester liquors separated from the pulp at the digester and the screw presses. This fraction is further processed for recovery of pulping chemicals by a FluoSolids combustion process[10]. Figure 22 is a schematic representation of the pulping and paperboard operation. The cooked wood chips, after pressing, are slurried in large volumes of water during primary refining operation. The virgin pulp is then mixed with 60 tons per day of corrugated waste clippings and subjected to a final refining. The pulp is further diluted and cleaned in centrifugal cleaners, after which it is sent to the paper machine. On-machine washing is practiced, and as much as can be used of the machine white water is recycled to the primary refining and cleaning steps described above. This machine "white water" comprised the feed to the reverse osmosis system for both the pilot run and the trailer run. "White water" is a technical term for the effluent waters containing fibers which drain from the wire screens on the paper machine. In this mill the "white waters" are quite dark in color. The overall objective was to develop methods for closing the pulp mill and the paper machine water systems by total recovery of the dissolved solids in a concentrate stream and production of clean water for mill reuse in place of fresh water. Concurrently with the RO studies, the mill has been engaged in a program to increase direct recycling so as to obtain the maximum water reuse consistent with product quality and mechanical operations. The unmodified white water available during most of the pilot and field studies covered in this report averaged 0.8 to 1.0 percent total solids, but more recently the recycle

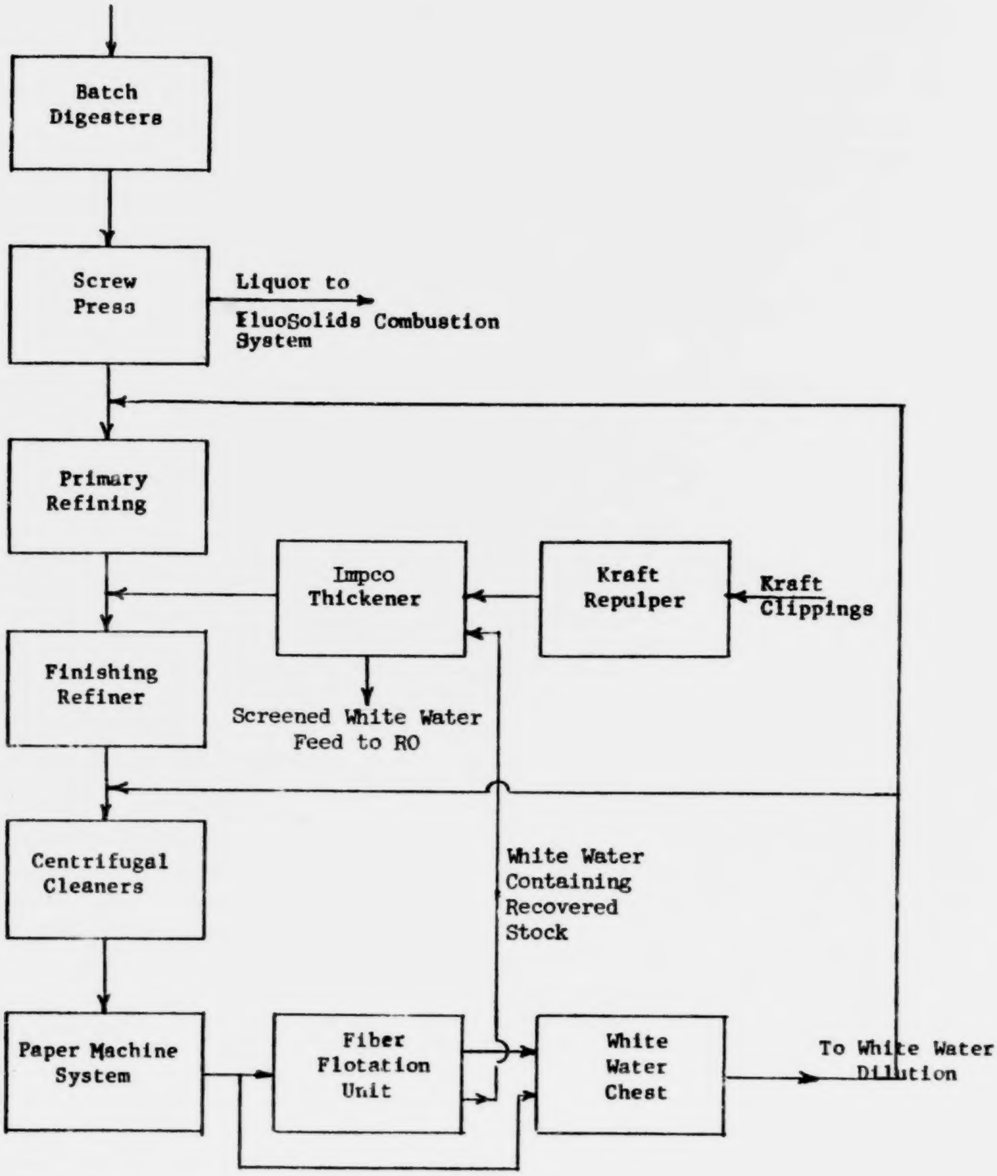

Batch Digesters
Screw Press
Liquor to FluoSolids Combustion System
Primary Refining
Impco Thickener
Kraft Repulper
Kraft Clippings
Finishing Refiner
Screened White Water Feed to RO
Centrifugal Cleaners
White Water Containing Recovered Stock
Paper Machine System
Fiber Flotation Unit
White Water Chest
To White Water Dilution

Figure 22. Neutral Sulfite Semichemical Pulping and Board Mill White Water System

waters have had a higher solids concentration, averaging greater than 3.5 percent total solids as of December, 1971. Morris, et al.[11] have summarized this recycle development program to date, including projections of planning for future RO processing at this NSSC pulp mill.

Small amounts of suspended fibers are present but these total solids mainly include suspended "fines" and colloidal suspensoids deriving apparently from ray cells with the dissolved solids. Analytical characterization of the screened paper machine white water recovered from the flotation unit and Impco thickener as feed to the RO unit at the time of this demonstration is summarized in Table 34.

TABLE 34

ANALYSIS OF A TYPICAL NSSC WHITE WATER FEED

Total solids, g/l	9.0
Sodium, mg/l	1075
BOD, mg/l	2340
COD, mg/l	9930
Optical density at 281 nm	51.8
Specific resistance, ohm-cm	350

Small Pilot Unit Study

Description of Equipment and Pretreatment Procedure

The small scale lab and pilot equipment for development of procedures for pretreatment and for reverse osmosis were similar to that used on Ca-base acid sulfite wash water at the first demonstration site. Nine new, Type 3, 18-tube modules, manufactured by Havens International and delivered early in 1968, were used to process NSSC white water obtained as filtrate from the thickener. The paper machine white water used as feed to the thickener was the underflow from the flotation unit. This fraction of the total white water, after clarification by passage through the mat of pulp on the Impco thickener, was collected for feeding to the RO process.

The thickener filtrate was discharged to a 40-mesh Sweco vibrating screen, with the filtrate running to a 150-gallon stainless steel tank, and then was pumped by centrifugal pump through a stainless steel heat exchanger, which cooled the filtrate from 48°C to 35°C for RO processing. The pH of this feed liquor ranged around 7.0 and further adjustment was not necessary. Temperature and tank level switches were mounted on the feed tank to shut off the pressurizing pump in case of high temperature or low level.

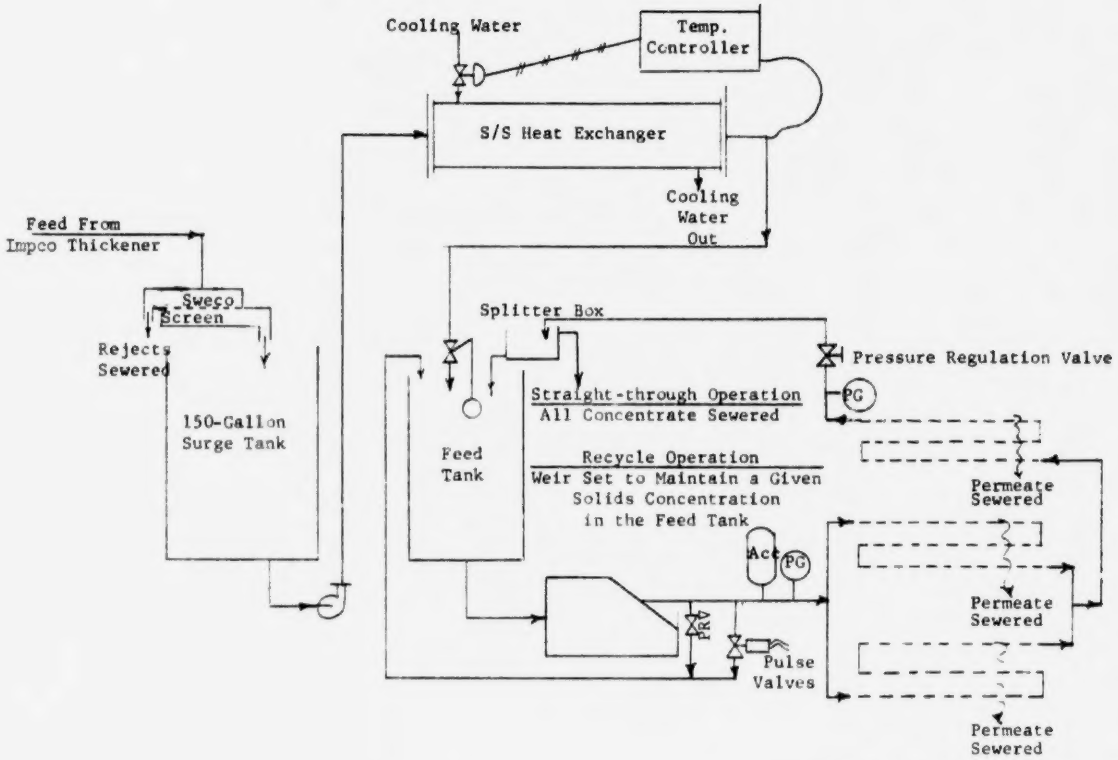
The pressurizing pump was a simplex, positive displacement, piston pump with infinitely adjustable stroke rated at 0 to 5.1 gpm at 745 psig. This pump discharged to the module system consisting of three banks, each with three 18-tube modules in series. The flow pattern was set up so that the flow from the simplex pump was fed into two of the banks in parallel, with the concentrate from these two banks combined to serve as the feed to the third bank of three modules. For the first part of the run with straight-through operation, the concentrate from the last of the modules in this bank was wasted to the sewer. To obtain a higher concentration in the last part of the run, a recycle feed and bleed system was set up, with the concentrate returned to the feed tank with a measured flow being drawn off from an adjustable weir device. The last bank was not used during the final 3 weeks of operation. Pressure fluctuations were dampened by a 1-gallon bladder-type accumulator at the pump discharge. System pressure was manually controlled by a spring-loaded pressure regulator. The system could be pressure pulsed with a preset time cycle by an electrically operated valve which relieved system pressure to atmospheric at the inlet side of the module system. Figure 23 is a schematic of the pretreatment and RO system for this phase of the study.

Data and Results – Preliminary Small Scale Runs

Reverse osmosis performance at feed solids concentrations between 1.0 and 9.3 percent was determined in two phases. The unit was operated first on a straight-through basis with a raw feed concentration of approximately 9.6 g/l for five weeks. Phase II followed with nine weeks of testing at various recycle rates to give performance indices for solids concentrations between 33-93 g/l. All tests were conducted with the feed solution of about 35°C, pH around 7, and pressures between 500-600 psig. Some of the modules developed leaks which decreased or ceased when the pressure was reduced. Later experience would seem to indicate that these leakages may have occurred at the sleeve-type seals for the individual tubes. Rupture of several modules occurred in the final weeks at 600 psig with pressure pulsing. The flux rate results are reported at the conditions of measurement and for comparative purposes, and also after adjustment to 600 psig and 35°C.

Inlet velocity to each of the two parallel banks was 2.4 ft/sec while operating with dilute feed on a straight-through basis. The loss of velocity within each stage of the system varied as the flux rate varied at the different concentrations. For the higher concentrations in Bank III, the velocities were between 3.3 and 4.3 ft/sec.

Throughout the run, the system was pressure pulsed for about 1 minute each hour. This pulse apparently provided a cleansing reverse flow back through the membrane by normal osmosis from the dilute permeate


Cooling Water
Temp. Controller
S/S Heat Exchanger
Cooling Water Out
Feed From Impco Thickener
Sweco Screen
Rejects Sewered
150-Gallon Surge Tank
Splitter Box
Pressure Regulation Valve
PG
Feed Tank
Straight-through Operation
All Concentrate Sewered
Recycle Operation
Weir Set to Maintain a Given Solids Concentration in the Feed Tank
Acc
PG
PRV
Pulse Valves
Permeate Sewered
Permeate Sewered
Permeate Sewered

PRV is a Pressure Relief Valve
PG is Pressure Gage
Acc is Bladder-Type Accumulator

Figure 23. Pretreatment and RO Operations for Processing NSSC White Water with Small Pilot Unit

side to the concentrate side. The permeate rate was measured 10 minutes before the pulse and 10 minutes after the pulse. The flux rate dropped about 12 percent between pulses, and average flux rates given are the arithmetical average of these two determinations. Samples taken at the time of each reading were composited over a week's operation.

Flux Rates and Rejections — Phase I — Straight-Through Operation

Measured flux rates averaged 11.3 gfd at inlet pressures between 491 and 500 psig for the dilute feed with an average solids concentration of between 11-14 g/l. This corresponded to a flux rate of 13.3 gfd when adjusted to 600 psig and 35°C. Flux rate averaged 10.4 gfd before pressure pulsing and 12.3 gfd after pressure pulsing for the five-week run. The weekly average flux rates for the run are shown in Table 35.

Rejections were excellent, averaging 98.7 percent for total solids, 97.5 percent for sodium, 96.4 percent for BOD_5, 98.4 percent for COD, 99 percent for optical density at 281 nm, and 94.5 percent based on conductivity. The only pretreatment required was screening through a 40-mesh screen and temperature adjustment to safe operating range for the cellulose acetate membranes (below 40°C). The modules were washed with water to protect the membrane while standing idle over the weekend after five or six days of operation, but the daily flux rate history (see Fig. 24) indicates that no irreversible flux loss occurred over a weeks operation. The reader is referred to Section VIII for a subsequent study on optimizing the RO system while processing NSSC white water.

Flux Rates and Rejections — Phase II — Recycle Operation

The flux rate data at feed concentrations between 38 and 103 g/l total solids are plotted in Fig. 25. The flux rate of 13.2 gfd at 600 psig and 35°C at 12 g/l solids decreased to 4.4 gfd at 600 psig and 35°C at 100 g/l solids. Most of the water (80 to 90 percent) to be removed overall was processed at relatively high flux rates ranging above 7 gfd. Rejections as shown in Table 36 remained uniformly high at all concentrations studied. This indicates the recycle system at higher concentrations was representative of a system processing this water in a staged, straight-through system such as would probably be used in large-scale operations.

Field Demonstration Studies with Large Trailer-Mounted RO Unit

The large 50,000 gallon per day trailer unit was operated on white water for a total of 593.5 hours. Liquor processing and equipment maintenance problems caused many delays and seriously hampered process evaluations. Interpretation in terms of performance which might be expected in a commercial unit processing this waste water is best obtained from evaluating operating data from the overall studies on both the small pilot

TABLE 35

FLUX RATE DATA

NSSC WHITE WATER WITH THE SMALL PILOT UNIT

Week No.	Av. System Concentration, g/l solids	Feed Temp, °C	Average Inlet Pressure, psig	Before Pulse, gfd	After Pulse, gfd	Average gfd	Av. Adj.[a], gfd
1	11	35	491	10.5	13.1	11.6	14.6
2	12	35	515	10.6	12.4	11.5	14.2
3	14	35	540	10.2	12.1	11.2	13.1
4	11	36	560	11.2	13.2	12.2	13.4
5	14	36	550	9.5	10.8	9.9	11.5
Av. Straight-Through Flow	12	35.5	531	10.4	12.3	11.3	13.3
6	58	36	546	6.0	6.8	6.4	7.5
7	75	37	561	5.3	6.0	5.7	6.3
8	60	37	536	6.6	7.4	6.9	8.4
9	74	35	576	5.4	5.8	5.5	6.1
10	78	35	583	5.4	6.2	5.8	7.0
11	44	35	596	7.2	8.4	7.8	8.0
12	102	36	585	3.7	4.3	4.0	4.3
13	38	34	612	8.0	8.9	8.4	8.4
14	98	35	620	4.4	4.9	4.6	4.4

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[a] Adjusted to 35°C and 600 psig inlet pressure.

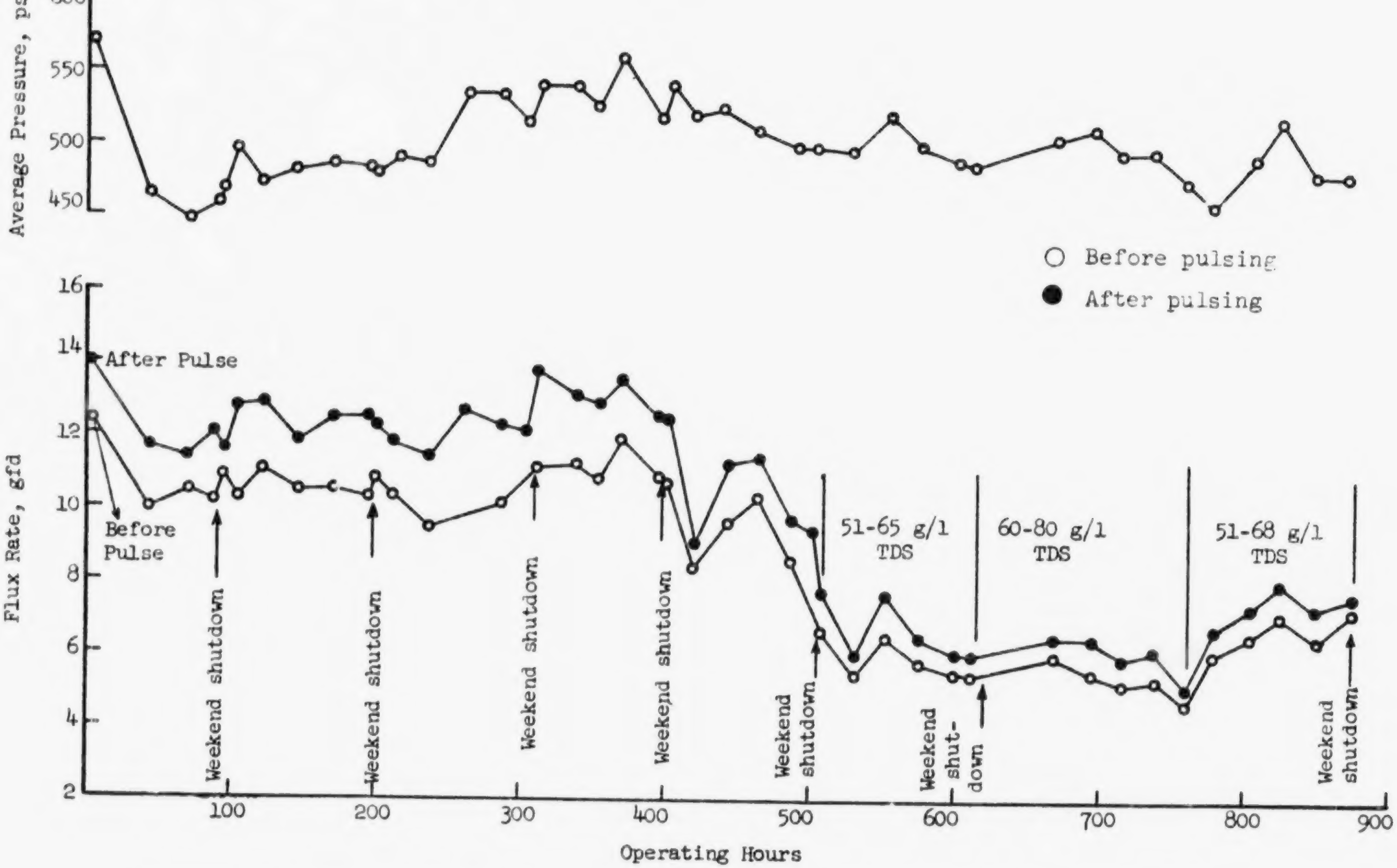

Figure 24. Daily Flux Rates and Pressures for Small Pilot Unit NSSC White Water

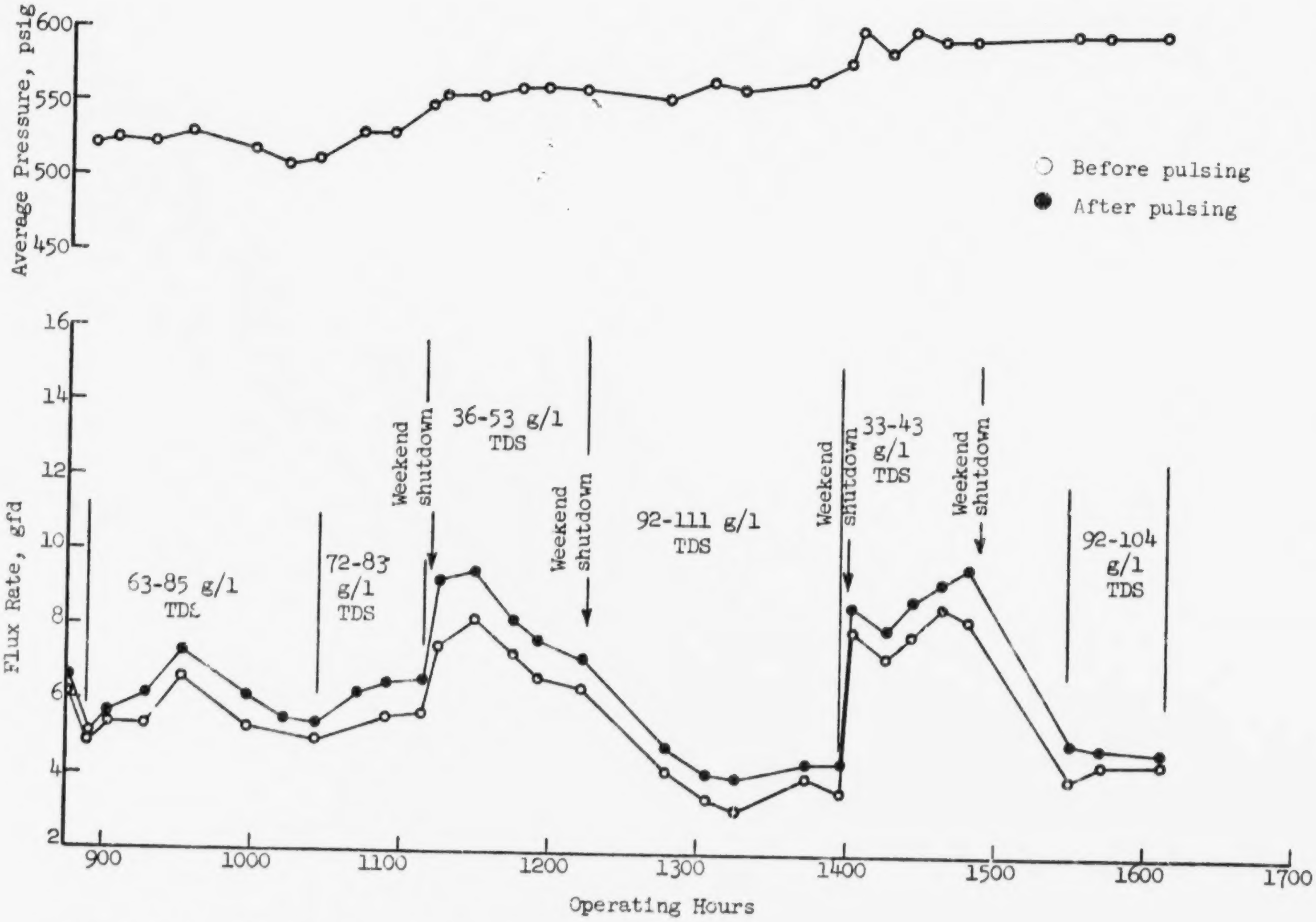

Figure 24 (Continued). Daily Flux Rates and Pressures for Small Pilot Unit NSSC White Water

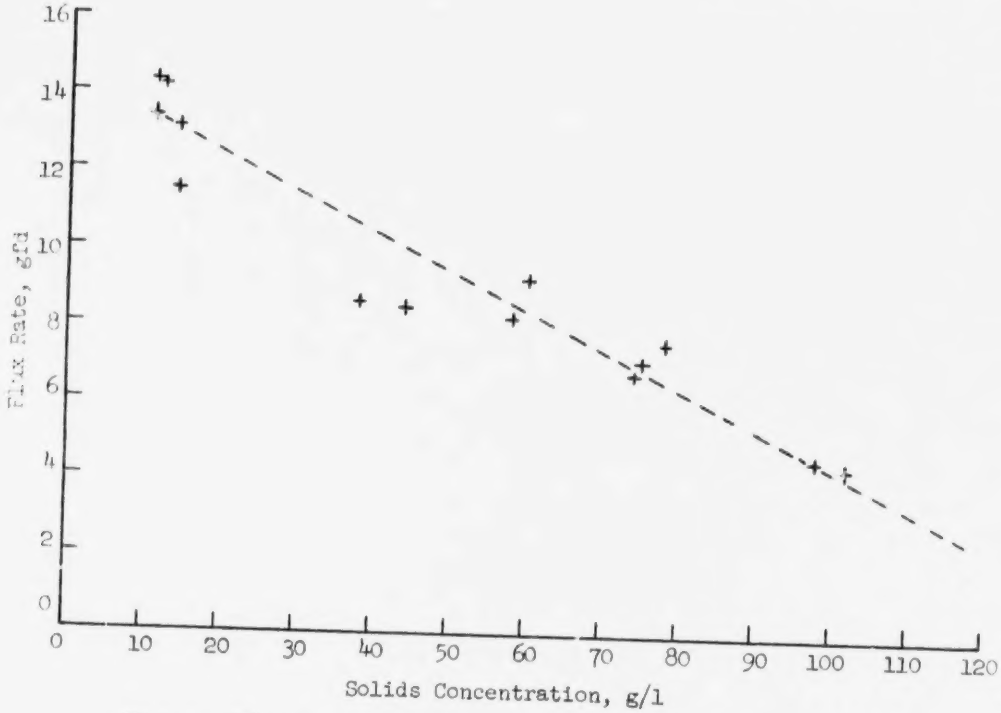

Figure 25 Variation in Flux Rates with Increase in Solids Concentration Processing NSSC White Water with Small Pilot Unit

and the larger field units. In both cases, product water quality was excellent, with exceptions occurring when faulty individual modules were obviously degrading the total flow. The final concentration during most of the runs was about 6 percent solids, and fell short of the desired 10 percent, but experience with both the pilot unit and short runs with the trailer unit shows that a 10 percent concentration can be reached feasibly. The overall flux rate for the trailer unit dropped to as low as 5.1 gfd. This indicates fouling occurred. However, subsequent studies with the trailer operating at higher velocities showed that overall flux rates of 7 gfd while concentrating from 1-10 percent solids could be maintained. These studies conducted at the Institute are reported in Section VIII

Equipment Description

A schematic of the auxiliary equipment installed for the trailer is shown in Fig. 26. The white water feed was obtained after passing through the thickener mat on the repulper system. This was then processed through a 40-mesh Sweco vibrating screen for final fiber removal as described for the small pilot study but with larger screen, tanks and piping. In initial tests, 100-mesh screens were tried, but these blinded frequently from slime growth. The 1000-gallon storage tank

TABLE 36

ANALYTICAL DATA AND REJECTIONS WHILE PROCESSING SEMICHEMICAL WHITE WATER WITH PILOT UNIT

Sample No.		Solids, g/l	Na, mg/l	BOD5, mg/l	COD, mg/l	OD, 281 nm	Specific Resistance, ohm-cm	pH
1	Feed	8.65	1020	2120	9120	47.0	630	7.48
	Permeate	0.18	36	64	210	0.74	7800	6.70
	Concentrate	14.06	1940	2920	[illegible]	125.0	348	7.05
	Rej., percent	98.4	97.6	97.5	98.2	99.1	93.7	
2	Feed	9.31	1250	1705	9990	50.0	385	6.35
	Permeate	0.16	33	48	191	0.60	7600	6.56
	Concentrate	15.79	2190	2780	16,560	82.0	250	6.45
	Rej., percent	99	98.1	97.9	98.6	99.1	95.8	
3	Feed	10.85	1420	2395	11,620	58.0	412	6.28
	Permeate	0.18	40	110	240	0.7	7300	6.58
	Concentrate	17.50	2290	3645	18,240	96.5	292	6.60
	Rej., percent	98.7	97.8	95	98.4	99.0	95.1	
4	Feed	8.24	1050	1770	8680	44	590	6.70
	Permeate	0.12	29	92	168	0.46	7800	6.00
	Concentrate	14.21	1770	2570	14,660	78	342	6.45
	Rej., percent	98.9	97.9	95.8	98.7	99.2	94.0	
5	Feed	10.70	1040	2420	12,000	60.0	387	6.70
	Permeate	0.23	50	157	294	0.90	5500	5.61
	Concentrate	16.54	1640	3770	17,660	89.0	258	6.50
	Rej., percent	98.3	96.3	96	98.0	98.8	94.1	
6	Feed	50.98	7700	11,200	55,000	320	137	5.40
	Permeate	0.81	233	485	794	1.70	1560	5.30
	Concentrate	65.0	9500	15,950	81,300	400	97	5.50
	Rej., percent	98.6	97.1	96.4	99.0	95.5	92.5	
7	Feed	60.60	8200	14,450	67,750	350	142	5.88
	Permeate	1.06	284	644	1061	1.82	1420	5.65
	Concentrate	90.84	12,100	20,950	105,600	575	127	5.95
	Rej., percent	98.6	97.2	96.4	98.8	99.6	90.5	
8	Feed	51.17	7300	12,450	56,650	255	155	5.95
	Permeate	0.68	194	424	665	1.52	1950	5.59
	Concentrate	67.87	9400	16,200	74,500	400	134	6.10
	Rej., percent	98.9	97.7	97	99.0	99.5	92.6	
9	Feed	63.35	10,000	15,500	70,950	371	156	6.30
	Permeate	1.08	275	590	835	0.99	1980	6.20
	Concentrate	85.24	12,300	20,750	88,400	475	139	6.55
	Rej., percent	98.5	97.5	96.8	99.0	99.8	92.5	

TABLE 36 (Continued)

ANALYTICAL DATA AND REJECTIONS WHILE PROCESSING SEMICHEMICAL WHITE WATER WITH PILOT UNIT

Sample No.		Solids, g/l	Na, mg/l	BOD$_5$, mg/l	COD, mg/l	OD, 281 nm	Specific Resistance, ohm-cm	pH
10	Feed	72.79	9500	14,250	71,450	385	215	6.35
	Permeate	0.96	259	570	868	1.09	1750	5.50
	Concentrate	83.24	11,500	18,500	88,500	490	182	6.55
	Rej., percent	98.8	97.5	96.5	98.9	99.8	88.7	
11	Feed	36.97	4100	8675	39,900	206	372	6.53
	Permeate	0.44	107	252	418	0.65	3650	5.72
	Concentrate	53.32	5700	13,300	57,600	294	350	6.57
	Rej., percent	99	97.8	97.7	99.1	99.7	89.8	
12	Feed	92.62	13,500	18,475	106,700	581	42	6.85
	Permeate	1.22	293	829	1279	1.05	978	5.81
	Concentrate	111.57	13,500	20,850	117,800	641	42	6.87
	Rej., percent	98.8	97.8	95.8	98.9	99.8	95.7	
13	Feed	32.97	4200	6850	37,900	195	96	6.62
	Permeate	0.37	125	216	414	0.67	3100	5.88
	Concentrate	42.65	5200	8975	51,200	222	82	6.82
	Rej., percent	99.0	97.3	97.3	99.1	99.7	97.1	
14	Feed	92.92	10,000	19,375	101,500	490	42	6.28
	Permeate	1.25	303	920	1346	1.15	842	5.35
	Concentrate	104.19	11,720	34,000	117,200	555	42	6.25
	Rej., percent	98.7	97.2	95.8	97.7	99.8	95.0	

was equipped with a low level capacitance probe interlocked with the trailer controls and with a bubble pipe connected to a valve on an emergency make-up line providing white water clarified by the flotation unit.

The feed was pumped from the tank with a Worthington centrifugal pump which brought the pressure to about 37 psig; the feed then made a single pass through the heat exchanger. City (Lake Michigan) water was the coolant; the discharge temperature was sensed by a capillary bulb and fed to a pneumatic transmitter, which in turn supplied a standard recorder-controller. The latter actuated the cold water supply valve. The feed pressure to the trailer was about 23 psig.

A second tank was utilized for collection of the concentrate (effluent) from the trailer; on occasions when the system operated smoothly and the concentrate solids content was high, this stream was pumped to the pulp mill liquor collection system for eventual incineration in the FluoSolids recovery plant.

The trailer described in detail in Section VI required only connections for power and the five liquid streams — feed, concentrate, product

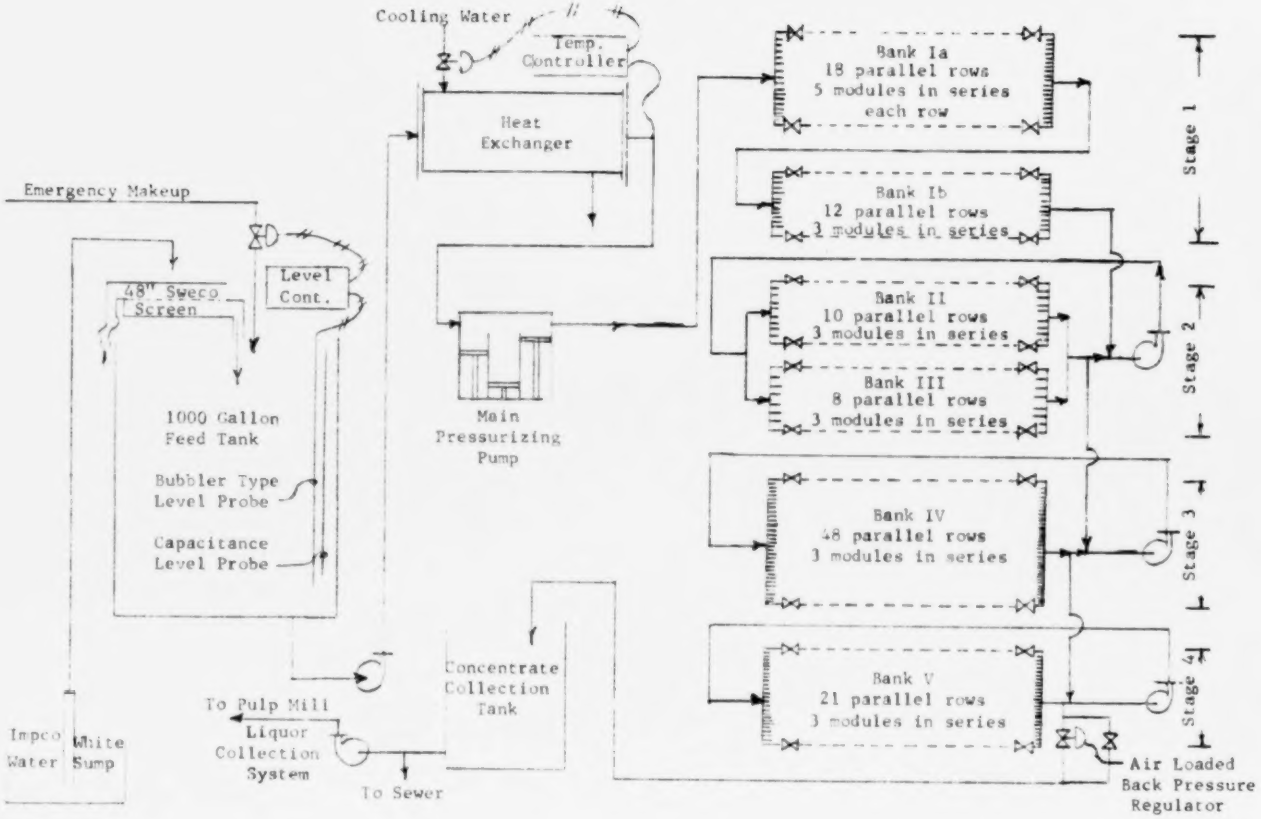
Cooling Water
Temp. Controller
Heat Exchanger
Emergency Makeup
Level Cont.
48" Sweco Screen
1000 Gallon Feed Tank
Bubbler Type Level Probe
Capacitance Level Probe
Main Pressurizing Pump
Bank Ia
18 parallel rows
5 modules in series each row
Bank Ib
12 parallel rows
3 modules in series
Bank II
10 parallel rows
3 modules in series
Bank III
8 parallel rows
3 modules in series
Bank IV
48 parallel rows
3 modules in series
Bank V
21 parallel rows
3 modules in series
Stage 1
Stage 2
Stage 3
Stage 4
Air Loaded Back Pressure Regulator
Concentrate Collection Tank
To Pulp Mill Liquor Collection System
To Sewer
Impco Water
White Sump

Figure 26. Schematic of Reverse Osmosis Pretreatment and Trailer Equipment

(clarified) water, city water, and floor drain. The 387 Type 3 modules in the trailer were arranged in five stages with a particular pattern throughout the tests. Banks II and III were operated in parallel, although the piping arrangement permitted an alternative series configuration. For almost all tests, the full complement of 387 modules (6579 square feet of membrane surface) was used.

A Manton-Gaulin piston pump with a variable-speed drive provided initial pressurization. Centrifugal pumps in each of the last 3 stages were utilized to restore pressure losses and to provide for the high velocity recirculation necessary to prevent fouling on the membrane surface. The centrifugal pumps were conventional with the exception that the casings were built for a high inlet pressure and specially designed mechanical seals were required in place of the usual packing on the shaft.

The restriction routinely in use for controlling back pressure at the concentrated end of the process flow was a manually-adjusted ball valve; a gas-loaded back pressure valve was also available but not used because of slower, less sensitive response during frequent startups and shutdowns.

The product water from each row flowed to a common header for the particular stage; the flows were then combined before being discharged.

All liquor lines were equipped with flowmeters of the magnetic follower type, having a spindle-mounted rotameter plug inside the pipe; these were quite inaccurate since the presence of slime introduced an obvious but indeterminate error. Pressure gages and temperature devices were located throughout the system but the capillary lines were subject to pluggage because of the suspended solids content of the liquor. Visual rotameters were installed on the product water lines and proved satisfactory.

The electrical system usually worked satisfactorily. A timer system had been incorporated to permit a "pulse" or rest period in which the unit would be depressurized. Because the small pilot unit of 1968 had many ruptures which may have been attributable to the "hard" abrupt pulse, and for mechanical simplification, the trailer was provided with a system in which depressurization was relatively gradual. Shock and hammer were not apparent in the system.

Operations

The unit was operated at pressures over 300 psig for 623.75 hours, of which 593.5 hours were on white water. There were five runs on white water including 4 principal periods of operation and one brief run; interspersed were periods of cleaning and testing.

Testing – 2/24 – 3/10

Checkout, modifications and brief runs on city water and white water during startup.

Run #1 – 3/11 – 3/15

For the first two days various problems, e.g., ruptured modules, caused interruptions. During the next three days the flux rates were declining sharply. Plugged rows were encountered in Bank V. Since the plugging or fouling was continuously causing increased pressures, it was decided to terminate the run after 88.75 hours.

Testing – 3/16 – 4/7

A program of evaluation and cleaning took place. After flushing the system with a detergent solution, the flux rate for every row was checked with city water. Since low flux rates indicated possible plugging on the liquor side, all 117 rows were checked for liquor flow. The unit was then operated with a 500 mg/l salt (NaCl) solution for feed to check for abnormal salt content in the product water for each row. Simultaneously the flux rates were measured on individual rows.

Since the flux rates were still low, cleaning was performed by circulating a neutralized solution of the sodium salt of EDTA (ethylenediamine tetraacetic acid). Following this treatment of all banks, a flux rate check was made with water; this indicated further cleaning was required. The cleaning was repeated on Banks I and IV, following which the flux rate check indicated that most modules were again clean.

Run #2 – 4/8 – 4/18

A new run began with white water, but again minor problems – ruptures, temperature surges, mill downtime, continuous pressure rise, etc. – caused many interruptions. There was little information on steady state operations; consequently, the unit was shut down until personnel were available for 24-hour coverage. Operating time on white water was 217.5 hours during this run.

Testing – 4/19 – 4/27

Maintenance was performed on the Manton-Gaulin pump, and other minor problems were corrected. Flux rate check was made with city water.

Run #3 – 4/28 – 5/4

With personnel assigned to every shift, the unit was operated on white water for 142 hours, of which 121.25 hours were in a continuous run. One interruption occurred that was later determined to be a problem in the main pump electrical drive system. Other minor disturbances, such as ruptured modules, were corrected as they arose. During the long run, the flux rate again deteriorated.

Testing – 5/5 – 5/18

Minor maintenance problems were corrected. One module was removed from each row in a section of Bank Ia (18 total) and from each row in Bank V (21 total) to reduce the pressure drop in later tests. A flux rate check was again made with city water.

Run #4 – 5/19 – 5/25

Again with personnel on all shifts, the unit was started up on white water and operated 139 hours. To determine the effects of slime, velocity, and flux regeneration resulting from downtime, the run was divided into three major sections:

> With some rows blocked off to increase velocity through the remaining rows and with 20 mg/l slimicide present in the feed, the unit was operated for 44.25 hours; a failure in the main pump electrical drive system occurred after 25.75 hours, however. The run was terminated when a booster pump seal failed. The unit was flushed with water and remained down until repairs could be made on the pump.
>
> Operations were resumed with the same rows still blocked off to maintain the high velocity, but with no slimicide in the feed. This run proceeded for 44 hours.
>
> Operations continued with the same number of rows in operation, but about every 50 minutes the rows in each stage were rotated, i.e., idle rows were put into service and a comparable number were taken out of service. Again, no slimicide was used in the feed. This method of operation continued for 49.25 hours.
>
> The unit was run for an additional 1.5 hours with all rows in service (no rotation) in an attempt to obtain higher concentrations.

The unit was then shut down and flushed.

Run #5 – 5/27

A brief run (5.75 hours) was made with white water to obtain samples at a high concentration, following which the unit was flushed.

Clean Up – 5/28 – 6/5

The flux rate was again checked with city water, following which the 39 modules removed for the final tests were reinstalled. The entire unit was then flushed with an EDTA solution and after checking the flux rate with city water, and further flushing with a solution with 20 mg/l algacide, it was disconnected and sent to the next demonstration site.

A detailed accounting of downtime is provided in Table 37 and shows the unit was operating on NSSC white water for 60.2 percent of the available operating hours.

TABLE 37

SUMMARY OF DOWN TIME FOR SECOND FIELD DEMONSTRATION
NSSC WHITE WATER

Period		Total Hours			Hours Lost Due to				Ruptured Modules[c]
From	To	Available	Operating	Lost	Pumps	Liquor[a]	Wash[b]	Other	
3/6/69	3/15/69	190	89	101	--	94	3	4[d]	7
3/17/69	4/7/69	136	0	136	--	--	104	32[e]	1
4/8/69	4/18/69	238	217.5	20.5	--	11	--	9.5[d]	9
4/19/69	4/27/69	40	0	40	16	--	8	16[f]	0
4/28/69	5/4/69	142.5	142	0.5	--	--	--	0.5[g]	6
5/5/69	5/18/69	80	0	80	--	--	24	56[h]	0
5/19/69	5/25/69	152.5	139	13.5	13	--	--	0.5[d,g]	7
5/27/69	--	6	6	0					
Total		985	539.5	391.5	29	105	139	118.5	30[i]
Percent of available		100	60.2	39.8	2.9	10.6	14.3	12.0	
Percent of downtime				100	7.4	26.8	35.5	30.3	

---

[a] High temperature of mill shutdown.

[b] Includes flux checks with city water and 5000 ppm NaCl.

[c] Module failure did not cause system shutdown unless indicated.

[d] Module rupture.

[e] Meeting of staff and awaiting supplies.

[f] Module shortage.

[g] Trouble in main pump electrical system.

[h] Rearranged module flow pattern to reduce pressure drop.

[i] Does not include 24 "fouled" or "plugged" modules.

Data and Results

Samples taken for laboratory analysis were limited in number since the trailer was not operated over a wide range of conditions. The analyses generally were comparable to the information obtained during the pilot runs, but did not exhibit the same low variance from the mean values, due to interruptions in operation of the unit and to problems arising with the greater number of modules having various degrees of leaking, plugging, etc. The analytical data and rejections calculated by assuming that the concentration in the system is equal to the average of the feed and final concentrate are given in Table 38. In those cases where the concentration in the final concentrate was not determined analytically, it was approximated. These results agree closely with the data obtained from the pilot run. Table 39 gives recoveries of the constituents in the final concentrate as calculated from the rejections and recoveries provided in the previous table.

In general, the unit was operated at 525-550 psig on the main pump discharge, with a feed temperature of 32-34°C, producing a concentrated stream of about 5.1 percent solids, and with an overall flux rate of 6.0 gfd (see Table 40). Limited data indicated a flux rate of 4.9 gfd in concentrating a feed of 1.7 percent solids to 9.5 percent. The flux rate was substantially below that anticipated and was the subject of much investigation.

Deterioration of the flux rates, not readily apparent due to frequent shutdowns in early stages of operation, were plainly evident in the longer runs. However, the flux rates recovered quickly after a shutdown of 30 minutes or more. See Tables 40 and 41 for the summary of operating data and Fig. 27 for a chronological plot of flux rates. The reasons for flux rate recovery were not readily apparent, and were cause for much speculation. A 30-minute shutdown might, for instance, be sufficient for microbiological gas production to lift slimes from the membrane surface. Much more likely was the probability of normal osmotic flow taking place back through the membrane from the permeate side to the concentrate side to flush away accumulations of fine fiber and of large molecular weight organic solubles such as lignin from the membrane surface matrix. Recovery from membrane compaction was also considered to adequately fit the picture.

After the early runs in which the flux rate deteriorated so quickly, a sample of the fouling material was taken from a defective module. Chemical analysis showed a very high percentage of calcium. It was speculated that a skin of fouling was present on the membranes when the trailer was received from the calcium-based Interlake Mill, and that new fouling was accumulating on this "prefilter." Consequently, all modules were cleaned with a solution of EDTA, a chelating agent known to be effective on calcium ions. This cleaning resulted in an improvement in the water flux rate to a value close to the original. Immediately after restarting on white water, however, the flux rate again declined; it was partially recovered either by a down period of several hours in which it was postulated biological action could take place or by a longer rest (several days) with city water containing 20 mg/l fungicide.

Several techniques, such as variation in the frequency and duration of the pulse, produced no improvements. The frequent interruption of operations by ruptured modules, etc., prevented determination of the rate of deterioration and whether or not a plateau of stable operation

TABLE 38

ANALYTICAL DATA AND REJECTIONS WHILE PROCESSING
SEMICHEMICAL WHITE WATER WITH TRAILER UNIT

Sample No.		Water Recovery Percent	Solids, g/l	Na, mg/l	BOD, mg/l	COD, mg/l	Color	Specific Resistance, ohm-cm	pH	Specific Gravity
1	Feed	81	10.75	1210	2938	12,010	10,000	212	7.00	1.004
	Permeate		0.68	186	276	680	5	1338	5.78	
	Concentrate		57.57	2820				51.7	7.08	1.028
	Rej., percent		98	87.7	96.8	98.2	99.9+	90.1		
2	Feed	74	8.94	1030	2975	10,140	5000	240	5.75	1.005
	Permeate		0.63	184	488	680	10	1322	5.50	
	Concentrate		34.03	9000				40	6.05	1.039
	Rej., percent		97.1	96.3	92.5	97.1	99.8	89.4		
3	Feed	87	9.48	1045	2745	10,692	5000	257	7.22	1.005
	Permeate		0.58	143	312	560	7	1921	5.75	
	Concentrate		72.86	7440				48.9	7.00	1.033
	Rej., percent		98.6	96.6	97.1	98.7	99.9	92.0		
4	Feed	80	9.08	1075	2230	10,090	3500	261	7.40	1.004
	Permeate		0.36	92	214	377	10	2674	5.72	
	Concentrate		45.59	5800				66.20	6.70	1.021
	Rej., percent		98.7	97.3	96.6	98.8	99.9+	53.9		
5	Feed	76	9.35	1125	3040	10,510	5000	227	6.18	1.004
	Perm. I		0.15	37	104	194	5	6284	5.18	
	Perm. II/III		0.21	54	142	261	7	4228	4.90	
	Perm. IV		0.41	101	310	467	5	2189	4.72	
	Perm. V		0.98	257	642	893	8	936	4.92	
	Perm. Total		0.41	116	264	437	8	2145	4.75	
	Conc. I		14.46	1760	4313	14,920	6000	172	6.32	1.007
	Conc. II/III		17.01	2080	5046	18,400	8000	149	6.07	1.008
	Conc. IV		29.72	3440	9030	34,720	22,000	94.4	6.05	1.014
	Conc. V		38.39	4680	10,600	41,280	27,200	76.7	6.13	1.018
	Rej. I		99.2	97.4	97.2	98.5	99.9	96.8		
	Rej. II/III		98.8	97.4	96.7	98.2	99.9	96.5		
	Rej. IV		96.6	97.1	96.6	98.7	99.9+	95.7		
	Rej. V		97.5	44.5	93.9	97.8	99.9+	91.8		
6	Feed	72	10.08	1225	2908	11,310	5000	341	6.72	1.004
	Permeate		0.32	104	288	367	50	3068	4.78	
	Concentrate		36.52	4400				88.6	6.25	1.017
	Rej., percent		98.6	96.3	95.4	97.8	99.0	93.0		
7	Feed	79	7.91	925	2075	9070	5000	317	5.85	1.003
	Permeate		0.36	93	265	416	50	2812	5.38	
	Concentrate		38.34	4440				80.6	5.83	1.017
	Rej., percent		98.4	96.5	95.6	98.4	99.0	92.7		
8	Feed	87	7.38	905	1975	8420	5000	343	6.03	1.003
	Permeate		0.42	106	282	439	50	2438	4.97	
	Concentrate		58.66	6100				60.8	6.03	1.027
	Rej., percent		98.7	97.0	96.4	98.8	99.0	91.7		

TABLE 38 (Continued)

ANALYTICAL DATA AND REJECTIONS WHILE PROCESSING
SEMICHEMICAL WHITE WATER WITH TRAILER UNIT

Sample No.		Water Recovery Percent	Solids, g/l	Na, mg/l	BOD, mg/l	COD, mg/l	Color	Specific Resistance, ohm-cm	pH	Specific Gravity
9	Feed	86	8.90	1070	2230	10,020	5500	268	5.42	1.004
	Permeate		0.53	146	498	735	5	1839	4.75	
	Concentrate		62.37	7860				54.9	5.90	1.020
	Rej., percent		98.5	96.7	93.3	98.1	99.1	91.2		
10	Feed	91	5.72	660	1455	6530	4000	450	6.77	1.002
	Perm. I		0.15	30.5	98	187	35	8604	5.95	
	Perm. II/III		0.13	34.5	103	169	8	7886	5.60	
	Perm. IV		0.22	56	163	260	8	4641	5.33	
	Perm. V		1.11	281.5	610	929	25	917	5.80	
	Perm. Total		0.34	82.5	215	472	15	3028	5.65	
	Conc. I		7.53	1280	1860	8020	6500	352	6.45	1.0025
	Conc. II/III		10.26	1320	2560	10,920	10,000	267	6.32	1.004
	Conc. IV		28.49	3160	7510	28,600	20,000	112	6.28	1.015
	Conc. V		61.3	6040	15,630	78,100	40,000	61.4	6.23	1.025
	Rej. I		97.7	96.8	94.1	97.4	99.1	95.3		
	Rej. II/III		98.7	97.4	90.6	98.5	99.9	96.6		
	Rej. IV		99.2	98.2	97.8	99.1	99.9	97.6		
	Rej. V		98.2	95.3	96.1	98.8	99.9	93.3		
11	Feed	92	8.52	1170	2429	8670	6500	295	6.58	1.000
	Perm. I		0.14	36.5	118	198	3	7526	5.80	
	Perm. II/III		0.18	47.5	146	226	5	5753	5.55	
	Perm. IV		0.47	125.5	353	500	10	2033	5.35	
	Perm. V		1.03	269	601	939	15	959	5.55	
	Perm. Total		0.39	107	292	439	10	2416	5.45	
	Conc. I		12.76	1960	3160	13,340	10,000	220	6.45	1.001
	Conc. II/III		17.42	2180	3960	18,560	10,000	158	5.81	1.006
	Conc. IV		53.32	6160	13,520	69,050	30,000	65	5.86	1.022
	Conc. V		104.99	11,580	27,850	133,400	85,000	40	6.03	1.045
	Rej. I		98.6	97.7	95.8	98.2	99.9+	96.6		
	Rej. II/III		99	97.8	96.3	98.8	99.9+	97.2		
	Rej. IV		99.1	98.0	97.4	99.3	99.9+	96.8		
	Rej. V		99.0	97.7	97.8	99.3	99.9+	95.8		

could be reached. Hence, it was necessary to have technical personnel present to operate the unit around the clock for a week. This run was accomplished with only one interruption and did demonstrate the rate and extent of flux decline. During the run it was decided to "rest" or take out of service briefly every section of modules to see if the flux rate would be improved; this proved effective but again left unanswered the reason for the improvement.

A final run, with 24-hour coverage, was made to determine the effects of slime, velocity, and of module rotation (see Table 41). The flux rate again declined but much less sharply; it was evident that as many as four factors may have influenced the rate of fouling, including soluble organic foulants, $CaSO_4$ scaling, microbiological sliming and membrane compaction. The tests were too brief for determining the ultimate flux rate with the improved techniques, but they did demonstrate that the fouling could probably be controlled.

After all tests were completed, the trailer was again cleaned with EDTA, but the flux rate was not restored to the original value. This might have been expected because the fouling accumulation since the first

TABLE 39

CALCULATED RECOVERY OF FEED LIQUOR COMPONENTS CONCENTRATE FROM TRAILER UNIT

Sample No.	Water Recovery in Permeate, percent	Recovery in Concentrate, percent				
		Solids	Sodium	BOD_5	COD	Color
1	81	97	82	95	97	99+
2	74	96	95	89	96	99+
3	87	97	92	94	97	99+
4	80	98	95	94	98	99+
5	76	98	95	95	98	99+
6	72	98	95	94	97	99+
7	79	97	95	93	98	99+
8	87	97	94	93	98	99+
9	86	97	93	87	96	99+
10	91	96	91	89	96	99+
11	92	97	94	92	97	99+
Range	72-92	96-98	82-95	87-95	96-98	99+

EDTA cleaning was probably not due to calcium deposits, and the chelating agent would not affect it much.

Samples from some of the ruptured tubes were saved and surface accumulations were microscopically inspected. The brief examination indicated the presence of very fine pulp fiber bonded or reinforced with slime accumulations.

Flux rate checks were made on several occasions with city water feed; selected rows and modules were monitored on each check to determine variation in fouling. Table 42 is a summary of the test flux data taken at various intervals. Within the banks, there is evidence that the fouling was related to the flow pattern of the lines distributing the liquor. On an overall basis, there were several incidents of individual rows and modules fouling nonuniformly or even improving in flux despite a decrease in the overall flux. It seems significant that Bank 1.08_b operating at high velocity had consistently high flux rates. Because of the difficulty in developing adequate answers to the fouling problem during this second field demonstration, further studies were carried out as reported in Section VIII. Higher operating velocities were ultimately found to suppress the fouling by NSSC white water.

TABLE 40

SUMMARY OF OPERATING DATA REVERSE OSMOSIS TRAILER

	Average of Data for Dates Shown					
Condition:	3/11 – 3/15 Irregular Running	4/8 – 4/16 Irregular Running	4/28 – 5/3 Continuous (Personnel on Shift)	5/19 – 5/25 Continuous Evaluation of Velocity, etc.	3/11 – 5/25 Weighted Average of all Readings	Single Reading 5/27 Special Run for High Solids
No. of measurements	5	8	35	35	83	1
Main pump pressure, psig	506	529	548	532	537	560
Flux rate, gfd						
Bank I	6.7	6.5	6.5	7.4	6.9	7.4
Bank II/III	5.9	6.7	5.6	7.6	6.6	8.7
Bank IV	5.1	5.2	4.7	7.2	5.8	5.8
Bank V	4.9	4.7	2.8	4.6	3.9	3.6
Overall	5.7	5.8	5.1	7.0	6.0	6.4
Feed rate, gpm	32.7	31.3	29.0	28.2	29.1	29.0
Conc. rate, gpm	6.6	5.0	5.9	4.2	5.1	2.6
Feed, solids, percent	0.95	1.03	0.93	0.78	0.88	0.90
Conc., solids, percent	5.2	6.0	4.5	5.7	5.2	9.5

TABLE 41

COMPARISON OF SELECTED DATA REVERSE OSMOSIS TRAILER

Conditions	4/28 – 4/29	5/19 – 5/20	5/21 – 5/22	5/23 – 5/24
Velocity (see below)	Normal	High	High	High
Slimicide	None	20 mg/l	None	None
Rotation of rows	No	No	No	Yes
Data				
Hours	44	39.25[a]	45.25	47.50
No. data measurements	11	9	12	12
Main pump pressure, psig	537	547	529	547
Flux rate, gfd (Average)				
Bank I	6.8	7.8	6.3	8.1
Bank II/III	6.2	8.5	7.5	6.9
Bank IV	4.6	7.8	7.3	6.6
Bank V	3.3	5.3	4.3	4.3
Overall	5.4	7.6	6.6	6.8
Loss in flux rate/24 hr				
Bank I	1.1	1.0	1.1	0.2
Bank II/III	1.1	2.9	0.6	1.1
Bank IV	0.5	-0.4	0.5	0.8
Bank V	0.7	1.0	0.2	0.4
Overall	0.8	0.7	0.7	0.6
Velocity, gpm/row[b]				
Bank I	1.63	1.75	1.70	1.83
Bank II/III	2.57	2.92	2.78	2.69
Bank IV	1.92	2.23	2.14	2.13
Bank V	2.36	2.70	2.68	2.73

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[a] Control failure occurred after 24 hours; first two readings after failure omitted.

[b] The flow measurement devices are known to be inaccurate, but the relative values should be reliable.

Pumping Energy

The power consumption factor was checked during several periods of steady operation. The power required for the pumps and controls averaged about 13.1 Kwh per 1000 gallons of feed in this field demonstration on NSSC white water.

Mechanical Failure

During this demonstration a total of thirty modules (7.7 percent) failed by rupture out of 387 in operation; i.e., there was a failure in the fiberglass support structure resulting in a massive leak. These ruptures occurred at varying intervals and averaged once each twenty-one hours. The distribution of failures was proportionate to the number of modules

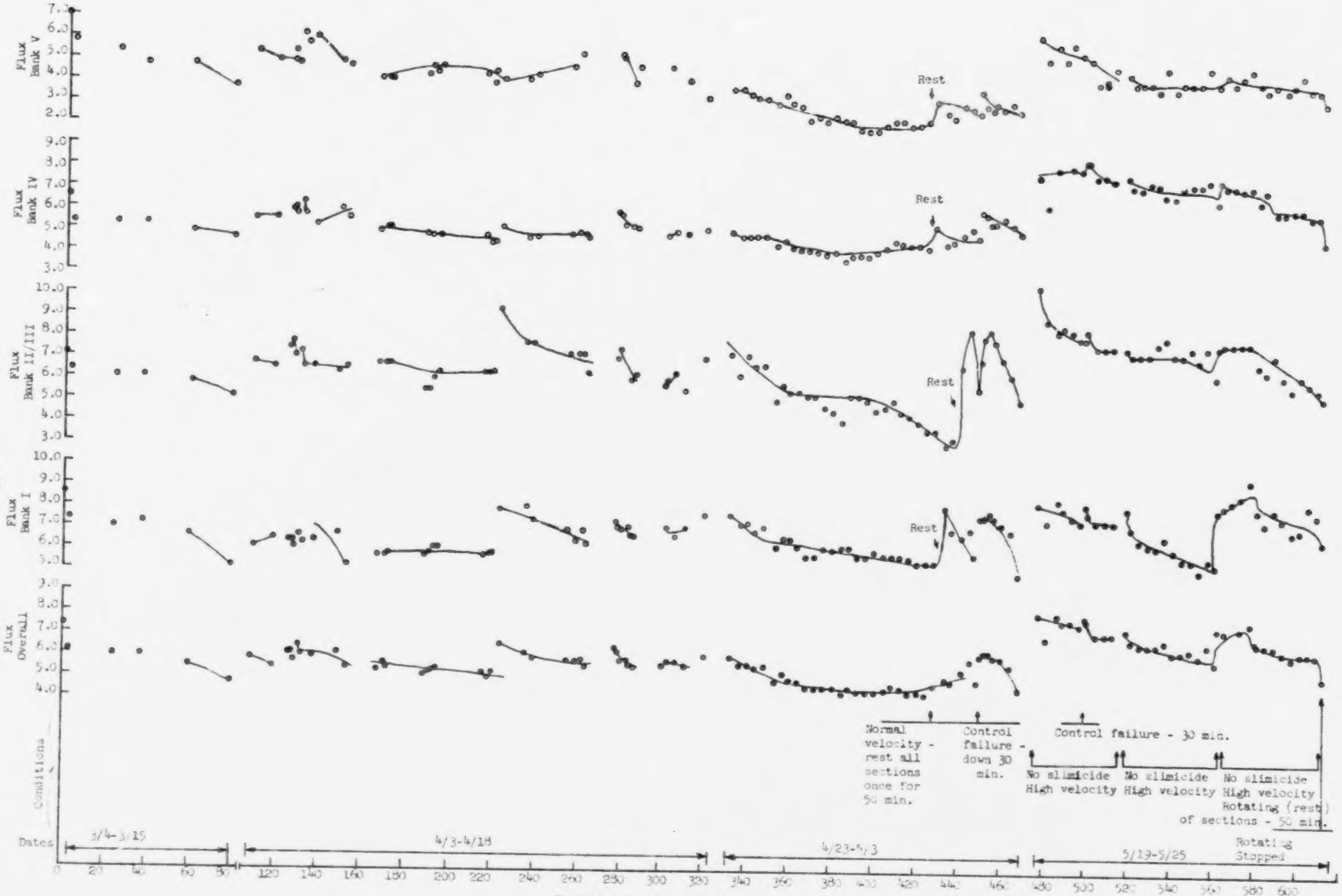


Figure 27. Flux (gfd) vs Operating Hours at Green Bay Packaging

TABLE 42

SUMMARY OF FLUX DATA FROM RECHECK TESTS

3/05/69 – Overall flux on trailer, with city water, was 15.9 gfd (25°C) at 550 psig

All remaining tests are gfd at 530 psig and 25°C

3/19/69 – City water, after 89.25 hours on white water
3/25/69 – 500 mg/l NaCl solution
4/04/69 – City water, after Versene wash of all banks
4/07/69 – City water, after Versene wash (2nd) of Banks I & IV
4/25/69 – City water, after 217.5 hours on white water (since Versene)
5/16/69 – City water, after 359.5 hours on white water
5/28/69 – City water, after 504.25 hours on white water
6/04/69 – City water, after Versene wash of all banks

Unit Measured	3/19	3/25	4/4	4/7	4/25	5/16	5/28	6/4
Trailer – Overall								
A – All at once			11.7		10.5	9.5	8.1	9.8
B – Computed from each bank at 530 psig	10.1	10.2	11.5	(12.9) From 4/4 and 4/7	10.5	11.1	8.2	10.6
Bank I	12.1	12.2	12.3	14.0	11.9	10.6/11.3	8.4/8.7	9.8/10.0
Row 1.04_a bottom	9.9	10.0					Out of	
Inlet module		11.3	12.5	15.1	12.2		service	12.7
2nd		9.3	10.3	13.0	7.7		4.0	5.6
3rd		7.8	9.0	10.9	7.3		3.3	4.9
4th		8.1	9.9	11.5	7.3		3.3	5.3
5th		7.8	7.7	11.1	6.5		3.7	5.3
Row 1.08_b Top	15.2	13.7						
Inlet module		14.6	15.7	17.0	16.3		12.6	14.1
2nd		9.3	12.8	14.1	13.5		12.3	13.0
3rd		13.1	15.7	16.7	17.1		15.6	16.2
Bank II/III	11.3	10.8	13.3		11.4	11.9	10.1	11.6
Row 2.09 Top	10.5	10.2						
Inlet module		8.5	12.1		13.7		10.9	13.8
2nd		8.8	12.1		13.4		11.2	14.1
3rd		11.1	14.0		12.6		11.8	14.5
Bank IV	8.7	8.0	9.7	12.1	9.7	11.4	7.8	11.7
Row 4.02 bottom	8.0	9.1		12.0	11.8		9.6	12.6
Row 4.03 top	9.0	11.1		15.5	15.1		10.8	14.8
Row 4.07 bottom	6.6	7.7		13.1	11.4		7.3	12.8
Row 4.11 middle	5.2	7.2						
Inlet module		5.5		8.7	7.8		8.0	13.3
2nd		6.2		10.8	10.5		9.7	13.6
3rd		6.7		9.8	8.2		5.8	10.4
Row 4.15 top	5.5	6.6						
Inlet module		4.2	6.4	8.8	6.1		3.3	7.1
2nd		4.6	5.8	8.5	8.2		6.3	10.4
3rd		7.9	10.7	13.6	12.9		11.7	14.6
Row 4.16 top	5.5	5.6		12.1	8.8		7.8	10.7
Bank V	8.4	10.6	12.3		9.1	8.7	7.8	8.9
Row 5.01 bottom	10.0	12.4	13.7		12.5		12.1	12.1
Row 5.05 bottom	6.5	8.0	11.5		9.0		6.8	9.5

in each stage. By a distinct margin, more failures occurred in the top rows of the sections than in the middle or bottom rows. Many of the modules were in tight groups of serial numbers, implying quality variations between lots of modules during manufacture. The soft pulse cycle in the trailer unit did not seem to reduce this module failure rate appreciably from the rate on the small units operated with a sharp "hard" pulse. However, most of the ruptures in the trailer did occur on repressurization after a pulse. Sustained mechanical stress or fatigue at points of imperfect manufacture probably accounted for these pressurizing failures.

There were some twenty-four incidents of plugged or severely fouled modules or rows of modules. Stripped membrane was apparently the primary cause of this type of failure. Very few plugged modules occurred in the bottom rows. Proportionately by stages, the fewest were found in Stage I and the most in Stage IV. A concentration effect may have contributed to the plugging problem.

SUMMARY AND CONCLUSIONS TO THE SECOND FIELD DEMONSTRATION ON NSSC WHITE WATER

The overall objective of this demonstration was to establish technical feasibility for employment of reverse osmosis as a key concentration step in closing the pulping and the paperboard machine effluent systems at this mill. Technical feasibility of this new and relatively untried unit operation could be considered well established. The demonstration further provided a base for advancing the development of answers to practical operating problems and for establishing the economics of reverse osmosis concentration.

The high quality levels of recovered water were well established and indicated the water can readily be recycled back to the mill for effective, trouble-free use in a closed recycle system. Clear, colorless water, free of foaming, sliming, and scaling problems of concern in mill operations can also be cited as having acceptably passed taste tests to many persons who have sampled the permeate.

Flux rates of water permeating through the membrane are a critical test of economic feasibility. A rate of 7 gallons per square foot of membrane surface per day was established in these demonstration trials. New and improved membrane equipment becoming available for tests as this project terminated in mid-1971 indicate substantially greater flux rates on the order of 10 gfd overall in concentrating from 1 percent solids to 10 percent solids seem attainable. It should be noted that 80 to 90 percent of the water to be removed in the 1 to 10 percent concentrating range is readily removed at high flux rates in the early stages on dilute feed. The flux rate decreases with increasing levels of concentration, but minimum flux rates of 5 gfd for the final 10 to 20 percent of the water recovery were demonstrated in these runs.

Flux rates were indicated to be dependent upon fouling characteristics. Techniques to reduce fouling problems developed during and after this demonstration depended especially upon maintaining certain minimum velocities, proportionately higher with increasing concentration level; and upon periodic pressure pulsing to permit cleaning of the membrane matrix by normal osmotic back flow.

Mechanical problems and liquor supply problems other than membrane equipment failure encountered during the demonstration reduced productivity of data and the attainment of desired, long continuous runs free of interruptions. Satisfactory answers to the mechanical operating problems seem capable of being developed in the normal course of perfecting the equipment used.

However, membrane life and reliability of membrane module supporting structures remain as the critical problems to be solved in establishing economics of the process.

The objectives of this mill program for recycling are discussed in more detail[2]. The economics of processing the liquor are further developed in Section X.

FIELD DEMONSTRATION NO. 3

CONCENTRATION OF AMMONIUM-BASE ACID SULFITE PULP WASH WATERS BY REVERSE OSMOSIS

This subsection describes laboratory and field studies for Demonstration No. 3 at the Oconto Falls, Wisconsin mill of Scott Paper Company. This was conducted as a feasibility study for concentration processing of ammonium-base acid sulfite pulp wash water with principal data and conclusions based upon use of the large-scale reverse osmosis trailer unit processing 50,000 gallons of pulp wash water per day.

A substantial amount of laboratory and pilot-scale field studies on the various types of dilute waste flows at this mill preceded the large-scale field demonstration. These preliminary tests evaluated possibilities for effectively processing the pulp wash waters, evaporator condensates, and the Ca hypochlorite bleach plant effluents collected from pulping and bleaching operations of the mill. It was concluded from these preliminary studies that the pulp wash water carried a relatively large portion of the total pollution load from the Oconto Falls mill. Effective complete treatment processing first required concentration of the dilute solutes. Subsequent studies were concerned especially with development of methods to process that flow by reverse osmosis to produce a concentrate for economic final processing and to recover clean reusable water for recycle to the mill.

This subsection includes the following areas of study:

Nature of the Ammonium-base Acid Sulfite Pulp Wash Water at Oconto Falls.

Possible Alternatives for Treatment of the Ammonium-base Acid Sulfite Pulp Wash Water.

Design of the Experimental Program.

- Laboratory Phases
- Pilot-Scale Field Studies
- Large-Scale Trailer Unit Field Studies

Data and Results

- Pilot-Scale Field Studies
- Large-Scale Trailer Unit Field Studies
- Summary of Large-Scale Trailer Unit Field Studies

Module Life Experience

Technical Feasibility of Reverse Osmosis Concentration

Supplementary Studies on Concentration Processing of Hypochlorite Bleach Effluent

Nature of Ammonium-Base Acid Sulfite Pulp Wash Water at Oconto Falls

Figure 28 provides a flow sheet for ammonium-base acid sulfite pulping and bleaching operations of the Scott Mill at Oconto Falls showing points of collection for effluents feeding to RO test equipment and indicates several possible areas for recovery and use or recycle of RO concentrates and permeates.

The Scott pulp mill at Oconto Falls produced 120 tons per day of bleached pulp (70 percent softwood:30 percent hardwood) at the time of making these field studies. Pulp wash water from this mill comprised a principal portion of the total pollution load on receiving waters as summarized in Table 43. Based upon the volumes and loadings indicated, the mill discharged 125,400 gallons per day of wash water containing 35,000 pounds of dissolved solids, 7800 pounds of BOD_5, and 750 pounds of ammonia daily. At this concentration the wash waters were found to have a temperature range of 43 to 48°C and a pH range of 2.8 to 3.0. Both pH and temperature may require some adjustment for concentration processing in the membrane equipment, which was limited to operation at temperatures not exceeding 40°C and within a pH range of 3.0 to 7.0. The feed liquor showed no evidence of containing pitch or scale-forming precipitates

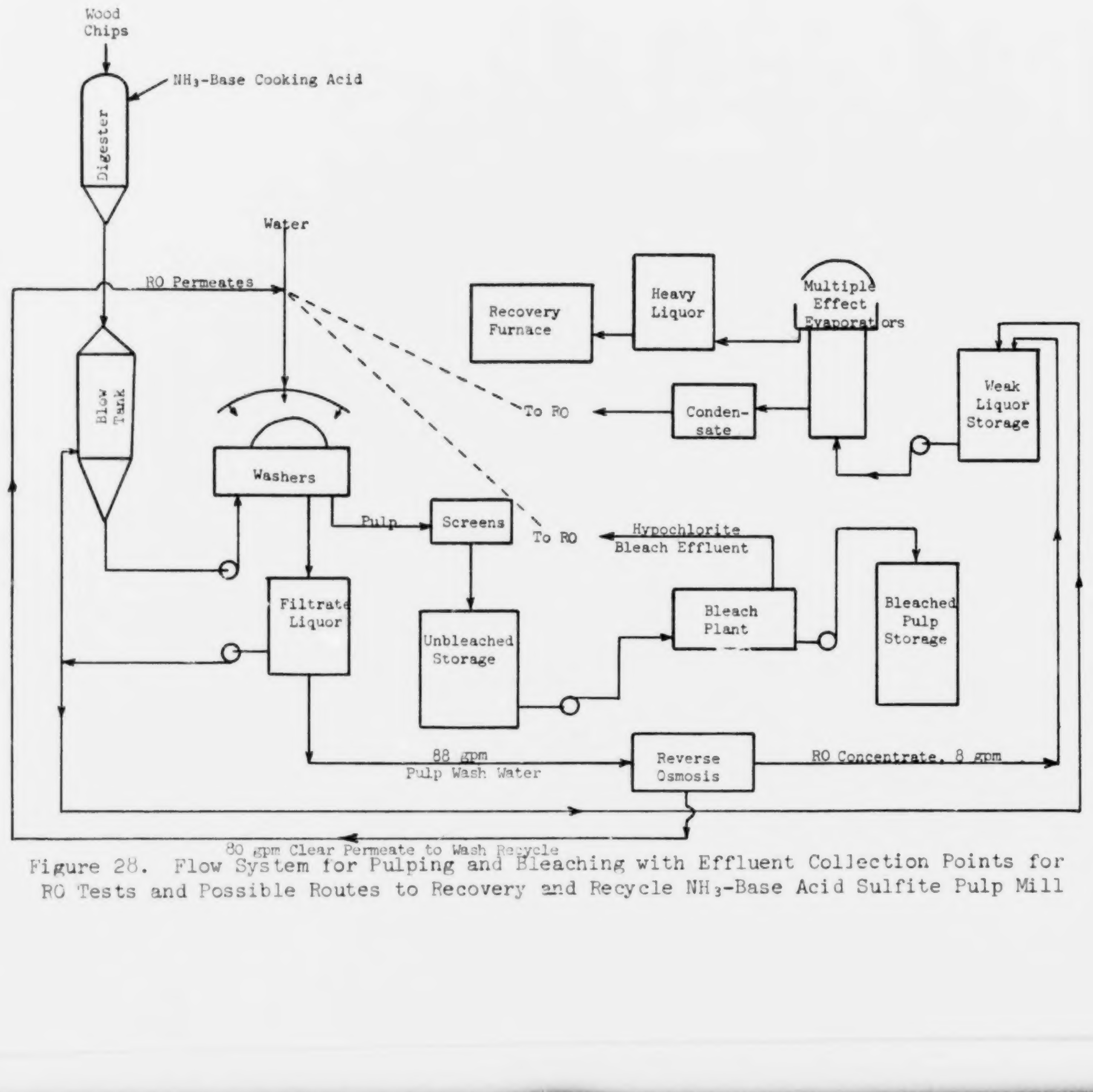

Wood Chips
NH₃-Base Cooking Acid
Digester
Water
RO Permeates
Blow Tank
Washers
Pulp
Screens
Filtrate Liquor
Unbleached Storage
To RO
To RO
Recovery Furnace
Heavy Liquor
Multiple Effect Evaporators
Condensate
Weak Liquor Storage
Hypochlorite Bleach Effluent
Bleach Plant
Bleached Pulp Storage
88 gpm Pulp Wash Water
Reverse Osmosis
RO Concentrate, 8 gpm
80 gpm Clear Permeate to Wash Recycle

Figure 28. Flow System for Pulping and Bleaching with Effluent Collection Points for RO Tests and Possible Routes to Recovery and Recycle NH$_3$-Base Acid Sulfite Pulp Mill

which were of concern in processing Ca-base softwood liquors in the first demonstration in Appleton. However, foaming was a serious problem in conducting the pretreatment steps for this ammonium-base liquor and careful design of mechanical handling equipment may be required in such steps as screening fiber from the liquor. Foam did not present a problem within the RO system.

TABLE 43

POLLUTION LOADING OF PULP WASH WATER
FROM THE AMMONIUM-BASE ACID SULFITE MILL

Discharge volume = 125,400 gallons per day
Discharged per ton of pulp = 1045 gallons
Pulp Production = 120 tons per day

	Concentration[a]	
Constituent	mg/l	lb/1000 gal.
Total solids	33,000	275
BOD_5	7,500	63
COD	50,000	417
NH_3	720	6

Temperature = 43 to 48°C (110 to 120°F)

pH = 2.8 to 3.0

---

[a] Based on average volume and 3.3 percent solids.

Possible Alternatives for Treatment of Ammonium-Base Acid Sulfite Pulp Wash Water

Unbleached pulp washings are a pollution control problem for most older pulping mills, but especially for those in the sulfite industry. In the acid sulfite mill, washings may originate from operations conducted in the digester, in blow tanks, and in subsequent washing and refining operations. The term "washings" in this mill refers to weak drainage produced after the strong liquor has been displaced in the blowpit diffusion washing step.

These trials for RO processing of pulp wash waters were undertaken at a time when various alternatives for treatment have been under consideration for development of practical answers to the pollution problem of this outdated and relatively small pulp mill. A preferred route for treatment involves reducing the quantity of pulp wash water as in newer modern pulp mills which usually involves large capital investment for installation of one of the various possible modifications of a staged or countercurrent washing system. A survey of suitably modified pulp washing systems is understood to be actively under way, and one or the other of these routes will probably be the chief competitor to possible employment of an RO concentration system. Much depends upon capital investment, and importantly also upon greatly reducing the operating charge for maintenance of the RO equipment, and importantly also upon greatly reducing the operating charge for maintenance of the RO equipment, as will be further discussed in Section X of this report.

Another alternative route to processing the pulp wash waters has been extensively studied in the microbiological oxidation processes by trickling filter, activated sludge, aerated lagoon, or even anaerobic treatment. Reduction of the BOD is, of course, the chief problem of immediate concern, but there are also other components in these pulp wash waters which could be expected to require further treatment within the next few years and beyond the capabilities of the biological oxidation processes in terms of removal of resistant organics and inorganics which would be incompletely treated, if at all by biological methods.

Search for other alternatives which could keep this mill in operation are understood to be under way. Many of the older acid sulfite mills facing this identical situation have already been shut down for lack of feasible answers in the past five years or so, and every effort is being made by mill management to avoid a final decision in that direction.

Design of the Experimental Program

Laboratory Phases

Substantial exploratory studies on RO processing of this pulp washing effluent were conducted in the central laboratory of the Effluent Processes Group at The Institute of Paper Chemistry prior to undertaking the field demonstration. As a further step in preparation for the field testing with the large 50,000 gallon per day unit, small pilot and the large-scale field demonstration units were installed and tested at Oconto Falls. Laboratory control and development studies were conducted concurrently with the field runs in Oconto Falls and also in confirming studies after these trials were completed. These laboratory studies were directed to first establishing the degree of pretreatment needed for successful operation of the reverse osmosis equipment:

> Gross amounts of fiber were removed by a screening step ahead of the membrane system. Preliminary work has shown that screens having a mesh of 40 to 120 per inch seemed to be adequate for keeping the check valves on the pumps and also the back pressure valves for the entire system from plugging by gross amounts of suspended matter. Small quantities of cellulose fiber had no apparent deleterious effect on operation of the tubular membrane

system. This was in contrast to the requirements for careful clarification and microfiltration steps required to eliminate plugging of capillary fiber and spiral-wound reverse osmosis systems which were conducted in preliminary tests in the Appleton laboratory as described in Section V.

Adjustment of the pH was necessary to have the feed liquor within the safe operating range of 4.0 to 7.5 for cellulose acetate membranes. Hydrolysis of the membranes may occur above and below that pH range. In order to prevent membrane hydrolysis, the feed liquor was neutralized to a pH of 4.0 to 5.0 with a commercial grade of sodium hydroxide.

Temperature adjustment was also required before reverse osmosis processing of the feed. When necessary, the feed liquor was cooled below 35°C with use of a tubular heat exchanger.

Foaming of the liquor was a substantial problem in the makeshift equipment available for pretreatment and required careful agitation and mixing of the liquor in the neutralization and fiber screening steps.

Fouling of the membrane surfaces continued to be an important concern in maintaining high-permeation rates of clean water. NH_3-base acid sulfite pulp wash water did not contain appreciable amounts of resinous or colloidal particulate matter. Therefore, no need was found for other pretreatment steps ahead of the reverse osmosis system. However, high degrees of turbulence and mixing were maintained across the membrane surfaces to minimize concentration polarization and membrane fouling effects.

Pilot-Scale Field Studies

Principal objectives in conducting the preliminary studies were to evaluate Type 3 Havens modules under conditions of straight-through continuous feeding, and at the same time to conduct controlled comparative study of flux rates for Type 4 and Type 5 membranes over an extended period of time. These studies became important because Type 3 modules installed for life study in Appleton laboratories showed a rapid decrease in flux rate under pressure. But the more dense structure of the Type 4 and Type 5 was reported to be less subject to compaction and usually did not show such a large initial reduction in product flux rate.

Fourteen Havens modules (four dense Type 5, one less dense Type 4, and nine relatively porous Type 3) were mounted on one of the pilot-scale Milton Roy pumping units. The Milton Roy main pressurizing pump was a duplex unit with each of the two pumps having an adjustable stroke length providing a variable flow of from zero to 173 gallons per hour and up to 1100 psig pressure. The pulp wash water was made up continuously by diluting digester strength spent liquor with well water to a level of about 1.0 percent solids. The temperature of the wash water was 12-14°C. The pH of the wash water was adjusted prior to reverse osmosis processing. The flux rate studies were made with straight-through continuous feeding. Both the concentrate and permeate were allowed to flow to the sewer after sampling. Limitations on pump size and the number of modules did not permit undertaking continuous concentration studies in these first tests.

Large-Scale Trailer Unit Field Studies

The objective for the larger scale studies was to demonstrate the capabilities of reverse osmosis systems in concentrating dilute pulp wash water to 10 percent or higher levels of solids under conditions of minimum recycling, and with the shortest possible holding periods of the liquor in process.

The large-scale trailer unit used for these studies was designed to process 20,000 to 100,000 gallons per day at a maximum operating pressure of 1000 psig. For this demonstration the trailer-mounted unit had 387 Havens 18-tube modules set up in five concentrating banks for processing flows at 50,000 gallons per day. Table 44 lists the arrangement of modules in each concentration bank for the demonstration at this mill.

TABLE 44

FIRST PERIOD ARRANGEMENT OF MODULES IN LARGE-SCALE
REVERSE OSMOSIS TRAILER UNIT
(June 9 to August 11, 1969)

	Number of		
Banks	Parallel Rows in Each Bank	Modules in Series in Each Parallel Row	Total Modules
Ia	18	5	90
Ib	12	3	36
II	10	3	30
III	8	3	24
IV	48	3	144
V	21	3	63

Operation of the trailer unit at Oconto Falls was beset by numerous difficulties. Aging and failure of the membrane modules was a growing problem in the seventh month of trailer operation. During the first period of 472 hours, some 63 of 387 modules were removed and replaced due mostly to tube failure and leakage. The trailer had been purchased with a one-year warranty, and accordingly the manufacturer arranged to repair and replace the original complement of modules. Trailer operation was halted on August 11, 1969 for removal of the modules. These were crated and returned to San Diego where new improved tubes and membranes were installed. The trailer unit was started again October 8, 1969 with 238 rebuilt modules. The modules configurations for the second period runs made during the month of October are given in Table 45.

TABLE 45

SECOND PERIOD ARRANGEMENT OF MODULES IN LARGE-SCALE
REVERSE OSMOSIS TRAILER UNIT
(October 1-17, 1969)

Banks	Number of Parallel Rows in Each Bank	Modules in Series in Each Parallel Row	Total Modules
Ia	15	4	60
Ib	10	2	20
II	8	2	16
III	8	2	16
IV	30	3	90
V	12	3	36

The arrangement of modules in each bank was modified for the purpose of maintaining adequate velocities at various levels of solids concentration. A successful run of 211 hours was possible with this modified set up of new modules within the 3-month contractual period of study. However, excessive failure rates were quickly apparent with these new modules after the first few days of the final period of operation.

Data and Results

The small pilot-scale field studies had been mainly concerned with the performance of Havens modules under conditions of straight-through continuous feeding. There was no attempt to study continuous concentration of the liquor because of limitations on size and availability of pumping equipment. Flux rate-concentration studies could be made with straight-through flows in the larger field demonstration trailer unit under conditions of minimum recycling and short holding periods for the liquor in process. The data and results of these comparative studies in the small and large units are reviewed in the following discussion.

Pilot-Scale Field Studies

The small pilot studies at Oconto Falls employed fourteen Havens modules of Type 3, Type 4, and Type 5 membranes. Pulp wash water at about 1.0 percent solid concentration was processed through the modules at 12 to 14°C and at 500 psig pressure. The temperature of pulp wash water was low because the feed liquor was made up by diluting digester-strength spent liquor with very cold well water. This reduced the original flux rates, since there was no arrangement for preheating the wash water before reverse osmosis. Velocities on the order of 3.0 to 3.5 feet per second were maintained throughout these studies. Readings of product flux, temperature, and pressure were taken daily. Samples of product water from each type module, as well as feed, were taken daily and composited weekly for analysis at the Appleton laboratories. These samples were analyzed for solids, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), ammonia-nitrogen (NH_3-N), calcium (Ca) and color. Percentage rejection ratios (R) were calculated using equation (4) in Section IV.

Table 46 gives the average flux rate and rejection data of pulp wash water for three weeks of continuous operation. Control tests permitted conversion of observed data to establish standards for temperature and pressure. Table 46 shows that the flux rates for relatively more porous Type 3 membrane modules averaged about 24 gfd when calculated at 35°C and 500 psig pressure. The flux rates of dense Type 4 and Type 5 modules varied between 9.0 and 14.4 gfd at 35°C and 500 psig pressure. The rejections of all components for Type 3 membrane were lower than the corresponding rejections of Type 4 and Type 5 membranes. Therefore, the higher flux rates in the case of the Type 3 membranes were at the expense of rejections.

Since the feed to this system was an ammonium-base sulfite wash water, it is interesting to note that very little ammonia was being transferred through the membrane. Most of the ammonia appeared to be bound to organics of sufficient molecular size to be well rejected. The relatively high concentrations of calcium in the feed reflect calcium carry-over from the wood and also the use of mineralized well water in the cooking and washing operations. All three types of membranes provided rejections above 95 percent for all the dissolved solids components, except for BOD_5, which ranged from 80 to 90 percent.

The small pilot unit installed at Oconto Falls encountered some problems with reciprocating pump failure due to piston scoring. This scoring appeared to be accelerated by the poor lubrication quality of the low pH wash water. There were several module failures in this straight-through feeding system, but all of them occurred in the older Type 3 modules. Most of these Type 3 modules were given to us during a period of module supply shortages and these had been used previously on high-viscosity tomato wastes. In addition, these modules had been transported between field trials in zero weather in an uninsulated truck

TABLE 46

FLUX RATE AND REJECTION RATIOS OF PULP WASH WATER SMALL PILOT UNIT

Total Solids of Feed Liquor = 1.5 percent
Average Pressure = 500 psig
Feed Liquor Temperature = 12-14°C
Average Flow Rate = 3.0-3.5 ft/sec

	Average Flux Rate Corrected at 35°C., gfd	Concentration, mg/l							Average Rejection, percent					
		Solids	BOD_5	COD	NH_3-N	Ca	Color	pH	Solids	BOD_5	COD	NH_3-N	Ca	Color
1st Week														
Feed	--	12,060	3555	14,753	280	91	2500	3.5						
Product water														
Type 3	25.2	563	510	719	2.8	2	15	4.0	94.3	85.5	95.1	99.0	97.8	99.4
Type 4	14.4	400	405	492	1.1	2	7.5	3.9	96.7	88.6	96.7	99.6	97.8	99.7
Type 5	9.0	387	326	352	0.7	2	5	3.9	96.8	90.8	97.6	99.8	97.8	99.8
2nd Week														
Feed	--	11,320	3820	15,160	220	84	2500	3.6						
Product water														
Type 3	24.4	580	672	838	2.6	2	10	4.2	94.9	82.4	94.5	98.8	97.6	99.6
Type 4	14.2	409	512	567	1.1	2	5	3.8	96.4	86.6	96.3	99.5	97.6	99.8
Type 5	9.0	382	474	544	0.7	2	5	3.9	96.6	87.6	96.4	99.7	97.6	99.8
3rd Week														
Feed	--	11,000	3195	14,260	246	81	2750	4.0						
Product water														
Type 3	23.0	504	605	749	--	2	7	4.2	95.4	81.1	94.8	--	97.5	99.7
Type 4	14.0	383	394	514	3.0	2	5	4.2	96.5	87.7	96.4	98.8	97.5	99.8
Type 5	3.8	340	336	476	1.0	2	5	3.9	96.9	89.5	96.4	99.6	97.5	99.8

Note: Color measurements were made on Hellige Aqua Tester (Color Comparator).
There were a total of 14 modules - 9 modules of Type 3, 1 module of Type 4, and 4 modules of Type 5.

and there was evidence of ice formation in the water contained in the modules in transit.

The results of this pilot study indicated that relatively high-flux rates, averaging about 24 gfd at 35°C and 500 psig pressure, could be obtained during processing of 1.0 percent solids wash water through Havens Type 3 membrane. The flux rates were actually measured at 12 to 14°C and the data were corrected to 35°C and 500 psig with use of established conversion factors. The rejections of Type 3 membrane were found to be above 95 percent for all components, except for BOD_5, which varied between 80 and 85 percent. It was concluded from these studies that Type 3 Havens membrane could be used effectively for the concentration of pulp wash water.

Large-Scale Trailer Unit Studies

The larger field demonstration studies at Oconto Falls were primarily concerned with obtaining data from straight-through concentration of pulp wash water to 10 percent or higher levels of solids in the multistage reverse osmosis trailer units. The first two months of operation were interrupted by the previously described mechanical and module failure problems. As a result of these problems, the data and observations are divided into two periods.

First Period — June 9 to August 11, 1969

The trailer arrived at Oconto Falls and was spotted adjacent to the sulfite mill on June 9, 1969. By June 17 substantially all equipment, including pumps and modules, were tested and ready for preliminary operation of the unit. The trailer unit was run for a total of 472 hours. In that brief period, some 63 out of 387 modules failed and were removed. The Sweco vibrating screen was overloaded and damaged, allowing a wood chip to pass through into the feed liquor. This was cause for blowing the packing in one cylinder of the feed pump. In addition, there were a number of brief shutdowns due to abnormally high feed liquor temperature, exceeding the capacity of the heat exchanger, failure of liquor supply from the mill, plugging of caustic lines, and failure of the pump which supplied caustic for adjusting the pH of the feed liquor. Wide variations were experienced in quality of the pulp washings, and this resulted in unusually high concentrations of total solids and in high temperatures of the feed stream at times. Overflow of hot, strong digester liquors into the wash water supply system was responsible for these feed quality problems, and, since such discharges sometimes lasted for most of a day, they forced the reverse osmosis unit to be shut down for corresponding periods (Table 47). However, the most frustrating aspect of operations was the increasingly critical problem of module failure from leakage of seals and rupture of the membrane support structures after some 7 to 8 months of operation during Demonstrations 1, 2, and 3.

TABLE 47

SUMMARY OF TRAILER DOWNTIME WHILE PROCESSING NH_3-BASE PULP WASH WATER

Period		Total Hours			Hours Lost for					Ruptured Modules[b]
From	To	Available	Operating	Lost	Pumps	Liquor[a]	pH	Wash	Other	
6/19/69	7/12/69	358	171	187	4	11	16	--	156[c]	7
7/14/69	7/18/69	- - - - Liner Sleeves for Cylinder Block in Main Pump Installed at Factory - - - -								
7/19/69	8/1/69	332	203	129	73	13	1	15	27[d]	26
8/1/69	8/12/69	151	92	59	3	11	--	22	23[e]	22
8/12/69	10/7/69	- - - - Modules of Series 1000 and 1100 Replaced with Rebuilt Modules - - - - - -								
10/7/69	10/17/69	226	211	15	--	5	--	--	10[f]	14
Total		1067	277	390	80	40	17	37	216	69[g]
Percent of available		100	63.4	36.6	7.5	3.7	1.6	3.5	20.3	
Percent of downtime				100	20.5	10.2	4.4	9.5	55.4	

---

[a] High temperature or shortage of liquor.

[b] System not shut down for module failures unless indicated.

[c] Search underway for new field engineer.

[d] New screen on pretreatment line and module failures.

[e] Module failures.

[f] Electrical problems.

[g] Does not include "leakers" (48) and "plugged" (3) modules.

Because of these frequent shutdowns, it became difficult to perform systematic studies, and few flux rate measurements could be made from sustained operation. Table 48 summarizes the key flux rate and operating variables in the data during this first period of operation. These data indicate that the average flux rates of the order of 8.0 to 10.0 gfd corrected to 35°C and 600 psig pressure, were obtained while concentrating the feed liquor from 1-2 percent to about 6 percent solids concentration. The average percentage of water removal during these concentration runs ranged between 66 and 74 percent.

Table 49 gives the rejection data for four samples collected during this first period of operation. The percentage rejection ratios are based on the average value of the concentrations of feed and concentrate. It is noted from Table 49 that the rejections were all above 94 percent, except for BOD_5, which varied from 76 to 95 percent.

During this period of June 9 to August 11, the trailer was operated for about 472 hours and experienced a number of shutdowns, mostly due to module failure. Little in the way of sustained and reliable data could be obtained as a result of these frequent shutdowns. It was, therefore, decided to replace all the original complement of modules. The trailer was shut down on August 12 and all the modules were shipped to the Havens factory in San Diego. Membrane tubes and seals in all of these old modules were replaced under the original warranty agreement. Shrouds, caps, and turnarounds which appeared to be in good condition were reused again in these modules. The newly refurbished modules arrived back in Oconto Falls in the first week of October.

Second Period — October 1 to October 17, 1969

During this second period, performance of a total of 238 rebuilt modules was compared to the original setup of 387 modules used in the first period of field trial at Oconto Falls and in the first two demonstrations. The arrangement of these rebuilt modules was modified in each staged bank of the trailer for the purpose of maintaining adequate velocities necessary to minimize concentration polarization and fouling of the membrane surfaces. By October 8, all the modules were tested and were ready for systematic concentration studies. These rebuilt modules had relatively high starting flux rates during the initial period, during which the membrane was compacting.

During this second period we had a successful run of 211 hours with relatively few module failures. Table 50 summarizes the flux rates and operating variables for each of the five concentration banks in terms of the number of modules, operating pressure, temperature, velocity, and overall percent recovery of water. Figure 29 plots corrected flux rate versus operating hours for these five banks operated as four stages. Banks II and III were run in parallel throughout these concentration runs.

TABLE 48

SUMMARY OF FLUX RATES AND OPERATING VARIABLES FOR NH_3-BASE ACID SULFITE LIQUOR

(June 9 to August 11, 1969)

Operating Hours	Average Operating Pressure, psig (P)	Average Feed Liquor Temp, °C (T)	Average Velocity, ft/sec	Concentration, g/l		Recovery of Water, Percent	Average Flux Rate at P, psig and T°C gfd	Average Flux Rate at 600 psig and 35°C gfd
				Feed	Concentrate			
171	400	23	2.5-4.0	21.9	64.4	66	4.4	10.0
273	480	29	2.5-4.5	12.4	60.2	79	5.5	8.5
472	590	26	2.0-4.5	14.0	54.0	74	6.3	8.0

Note: Tap water flux rate at zero hours = 13 gfd at 35°C and 600 psig average pressure.

TABLE 49

REJECTION DATA FOR NH_3-BASE ACID SULFITE LIQUOR
(June 9 to August 11, 1969)

Sample	Concentration, g/1						Specific Gravity	Color	Optical Density at 281 nm
	Neutral Solids	BOD_5	COD	Calcium	NH_3-N	pH			
I Feed	21.93	3.46	32.50	0.091	0.576	4.3	1.006	4500	220
I Permeate	1.74	1.60	1.36	0.000	0.024	4.4	--	15	2
I Concentrate	64.39	--	--	0.224	1.959	4.2	1.028	--	590
Rejection ratio, percent	96.0	76.5	97.9	100.0	98.1	--	--	99.9	99.5
II Feed	12.43	3.73	26.70	0.070	0.236	3.4	1.002	3500	126
II Permeate	1.40	1.31	2.05	0.001	0.043	3.9	--	25	21
II Concentrate	60.23	--	--	0.324	1.473	2.9	1.022	--	562
Rejection ratio, percent	96.2	88.0	97.4	99.5	95.0	--	--	99.6	93.9
III Feed	10.31	2.02	14.95	0.044	0.200	4.3	1.001	3500	113
III Permeate	0.66	0.53	1.07	0.004	0.023	4.5	--	15	10
III Concentrate	44.70	--	--	0.320	1.270	4.1	1.015	--	420
Rejection ratio, percent	97.6	85.0	97.3	97.80	96.9	--	--	99.8	96.3
IV Feed	18.80	5.76	25.00	0.093	0.431	4.3	1.005	5500	205
IV Permeate	0.68	0.65	1.08	0.001	0.023	4.8	--	25	7
IV Concentrate	63.43	--	--	0.361	1.490	4.9	1.023	--	626
Rejection ratio, percent	98.4	94.6	98.0	99.6	97.6	--	--	99.7	98.3

TABLE 50

SUMMARY OF FLUX RATES AND OPERATING VARIABLES FOR NH_3-BASE ACID SULFITE LIQUOR (October 1-17, 1969)

Operating Hours	Bank Ia and Ib No. of Modules in Operation	Inlet Velocity, ft/sec	Measured Flux Rate at P psig and T°C, gfd	Corrected Flux Rate at 600 psig and 35°C, gfd	Bank II-III No. of Modules in Operation	Inlet Velocity, ft/sec	Measured Flux Rate at P psig and T°C, gfd	Corrected Flux Rate at 600 psig and 35°C, gfd
4	64	3.7	9.3	12.9	32	3.0	8.2	11.1
10	80	3.5	8.6	12.1	32	3.4	7.2	9.7
14	80	--	8.4	11.8	32	--	7.7	10.4
17	80	--	7.2	10.1	32	--	7.2	9.7
36	80	2.7	7.4	10.4	32	3.7	7.2	9.7
41	80	1.9	7.0	9.9	32	2.9	6.4	8.6
109	80	--	--	--	32	--	4.8	6.4
187	80	2.6	5.6	7.9	26	2.7	4.2	5.6
205	80	2.5	5.6	7.9	36	2.9	4.9	6.6
211	80	--	6.3	8.9	36	--	4.7	6.3
Av operating pressure, psig (P)		515				537		
Av feed temp, °C (T)		27				27		
Av percent solids of feed liquor		3.1-4.1				4.1-4.9		
Av velocity, ft/sec		3.1				2.9		
Av flux rate at 600 psig and 35°C		9.0				7.0		
Overall percent of recovery water, percent		24				34		

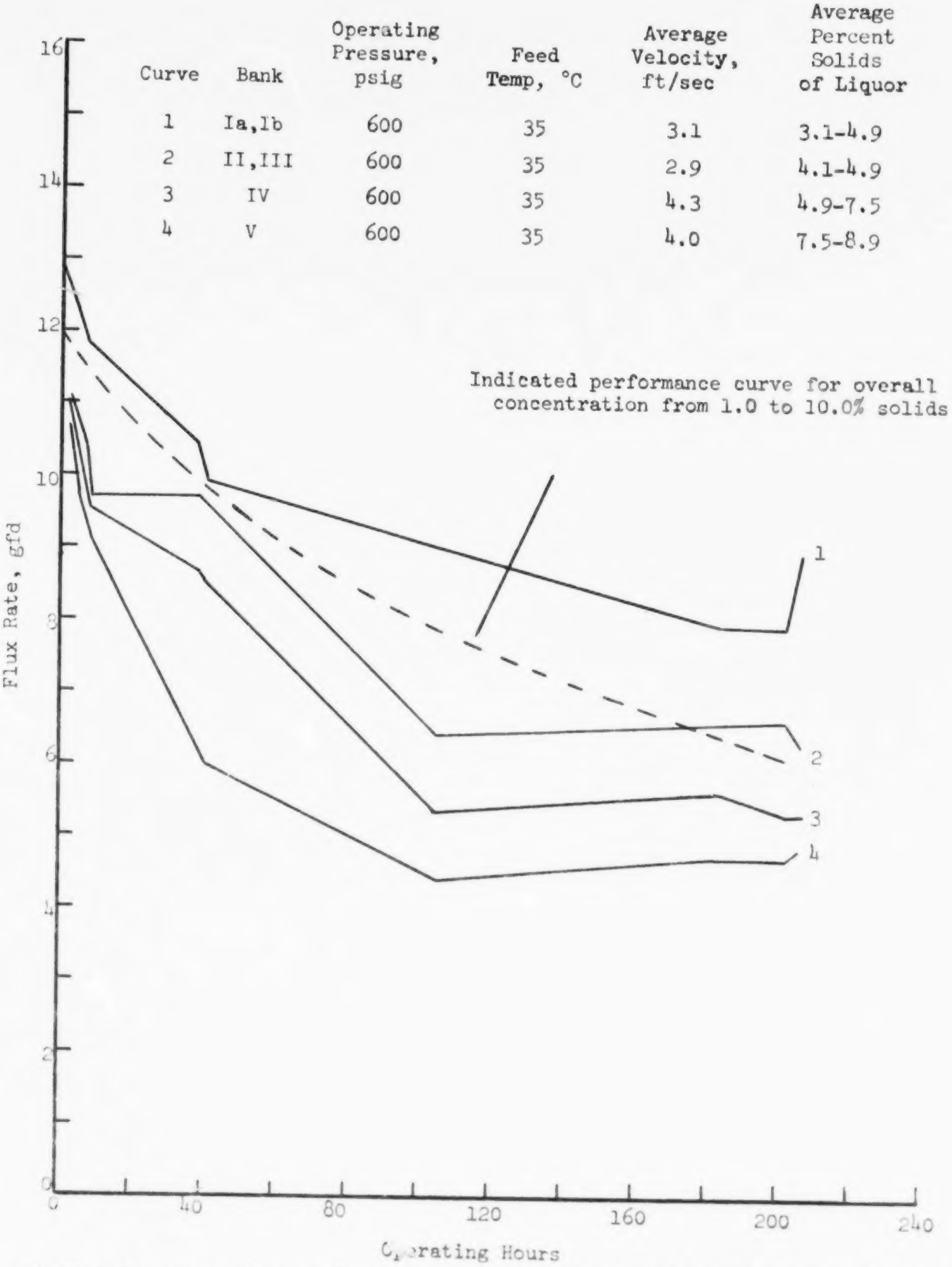
Table continued next page.

TABLE 50 (Continued)

SUMMARY OF FLUX RATES AND OPERATING VARIABLES
FOR NH_3 - BASE ACID SULFITE LIQUOR
(October 1-17, 1969)

	BANK IV				BANK V			
Operating Hours	No. of Modules in Operation	Inlet Velocity, ft/sec	Measure Flux Rate at P psig and T°C, gfd	Corrected Flux Rate at 600 psig and 35°C, gfd	No. of Modules in Operation	Inlet Velocity, ft/sec	Measured Flux Rate at P psig and T°C, gfd	Corrected Flux Rate at 600 psig and 35°C, gfd
4	81	3.9	9.2	11.0	27	4.9	8.5	10.7
10	90	4.8	8.5	10.2	36	4.1	5.4	6.8
14	90	--	8.1	9.7	36	--	7.1	9.0
17	81	--	8.0	9.5	27	--	7.2	9.1
36	81	5.0	7.2	8.7	36	4.2	7.5	9.5
41	81	5.0	7.1	8.5	36	4.2	4.7	6.0
109	90	--	4.4	5.3	27	--	3.5	4.4
187	90	4.1	4.6	5.6	27	3.8	3.8	4.7
205	90	4.0	4.4	5.3	27	3.6	3.8	4.7
211	90	--	4.4	5.3	27	--	3.8	4.8
Av operating pressure, psig (P)		595				575		
Av feed temp, °C (T)		26				26		
Av percent solids of feed liquor		4.9-7.5				7.5-8.9		
Av velocity, ft/sec		4.3				4.0		
Av flux rate at 600 psig and 35°C		6.0				5.5		
Overall percent of recovery water, percent		59				65		

Note: Tap water flux rate at zero hours = 13 gfd at 35°C and 600 psig average pressure.
Average flux rate in each concentration bank is calculated as the weighted arithmetic mean.



Curve	Bank	Operating Pressure, psig	Feed Temp, °C	Average Velocity, ft/sec	Average Percent Solids of Liquor
1	Ia,Ib	600	35	3.1	3.1-4.9
2	II,III	600	35	2.9	4.1-4.9
3	IV	600	35	4.3	4.9-7.5
4	V	600	35	4.0	7.5-8.9

Figure 29. Flux Rate vs Operating Hours — Ammonia-Base Acid Sulfite Liquor

During this run we again had substantial variation in the concentrations of incoming feed liquor to the trailer unit. At times the concentration of the feed was as high as 5 percent solids. It is noted from the data of Table 50 and Fig. 29 that average flux rates of the order of 5.5 to 9.0 gfd (or an overall flux rate of 7.0 gfd) were maintained at 600 psig and 35°C over a period of 211 hours. During this period, the average concentration of the feed liquor actually available was 3 percent solids and the feed was concentrated to an average level of 9 percent solids.

Figure 29 also gives the indicated performance for overall concentrations from 1 to 10 percent solids (the range intended for study in the original experimental design). This performance curve was determined by taking into consideration the percentage removals of water at various concentration levels, and shows an overall flux rate of about 8.0 gfd in the range of 1 to 10 percent solids concentrations. This was higher than that of 7 gfd in the range of 3 to 9 percent solids. The higher rate of flux at lower starting concentrations is to be expected since 80 percent of the water to be removed in the 1 to 10 percent solids range occurs in the early stages of concentration below 5 percent solids. (It should be noted that the average tap water flux rate of these Type 3 Havens modules was 13 gfd at 35°C and 600 psig pressure.)

Table 51 gives the rejection data for two brief periods of higher level concentration during this second period of operation. These two sets of samples were collected when feed concentration was as high as 5 percent solids, and the concentration of corresponding concentrates was about 13 percent solids. Here the rejection ratios are again based on the average value of the concentrations of feed and concentrate. The data in Table 51 indicate that the rejections of solids, COD, calcium and NH_3-N are all above 92 percent, whereas BOD_5 rejections average about 84 percent.

Summary of Large-Scale Trailer Unit Field Studies

During the first and second periods of trailer operations the unit was operated for a total of 683 hours. During that period about 1.2 million gallons of feed liquor was processed to produce 400,000 gallons of concentrate and 800,000 gallons of clean, reusable product water. The average flux rate throughout the concentration runs was about 7 gfd while concentrating the feed liquor from 3 to 9 percent solids and with 65 percent overall recovery of water. These flux rates were determined at 35°C and 600 psig average pressure. (The initial tap water flux rate of both old and new Type 3 Havens modules was 13 gfd at 600 psig and 35°C.)

Table 52 gives the recovery data corresponding to each of the six samples collected during the first and second period of operation. The data in Table 52 indicate that the percentage recovery of solids, COD, calcium, NH_3-N, and color were all above 90 percent, whereas the percentage recovery of BOD_5 averaged about 85 percent.

TABLE 51

REJECTION DATA FOR NH_3-BASE ACID SULFITE LIQUOR
(October 1-17, 1969)

Samples	Concentration, g/l						Specific Gravity	Color	Optical Density at 281 nm
	Neutral Solids	BOD_s	COD	Calcium	NH_3-N	pH			
V Feed	50.48	13.83	69.70	0.210	1.436	3.70	1.018	15,000	450
V Permeate	4.13	3.41	6.47	0.016	0.106	3.75	--	500	68
V Concentrate	135.91	32.37	176.20	0.528	4.022	4.10	1.054	--	1220
Rejection ratio, percent	95.6	85.4	94.7	95.7	96.1	--	--	98.2	91.9
VI Feed	47.23	12.45	65.90	0.218	1.578	4.45	1.017	12,500	436
VI Permeate	6.44	4.30	9.60	0.032	0.205	3.92	--	1,300	92
VI Concentrate	137.35	38.34	185.40	0.580	4.463	4.12	1.054	--	1256
Rejection ratio, percent	93.1	83.1	92.4	92.0	93.7	--	--	94.7	89.1

TABLE 52

RECOVERY DATA FOR NH_3-BASE ACID SULFITE LIQUOR
(June 9 to August 11 and October 1-17, 1969)

Sample	Operating Hours	Concentration, g/l solids		Recovery Ratio, percent					
		Feed	Concentrate	Solids	BOD_5	COD	Calcium	NH_3-N	Color
1	0-171	21.93	64.39	96	77	97	100	98	100
2	172-273	12.43	60.23	94	85	95	98	92	99
3	273-300	10.31	44.70	96	81	96	96	95	99
4	300-472	18.80	63.43	97	94	97	99	96	99
5	472-572	50.48	135.91	95	85	--	94	96	98
6	572-683	47.23	137.35	93	83	92	92	93	94

Note: Percent recovery ratio = $\left(\frac{\text{Concentrate flow rate x concentrate concentration}}{\text{Feed flow rate x feed concentration}}\right)$ 100.

The osmotic pressure of the NH_3-base acid sulfite liquor was relatively high compared to those of calcium-base acid sulfite and NSSC liquors, and varied from 125 psia at 10 grams per liter to 350 psia at 100 grams per liter solids concentration. The effective driving force determined from osmotic pressure data averages about 375 psia at 600 psig operating pressure within the range of 3 to 9 percent concentrations. Based on the average tap water flux rate of 13 gfd at 600 psig this effective driving force at 375 psi would have resulted in an average flux rate of at least 8 gfd. The overall average flux rate obtained during the entire operating period was 7 gfd which indicates that there probably was some fouling of the membrane surfaces. However, the unit was "pulsed" during the entire period by the automatic pulsing system programmed to shut down 2 minutes out of each hour. The pulsing proved to be helpful during this demonstration period, but it did not completely solve the fouling problem.

Fouling of the membrane was always a matter of concern in these pilot and trailer field studies. Therefore, special studies were made for determining the required degrees of turbulence and mixing necessary to minimize concentration polarization and fouling effects. These studies were made in the Appleton laboratories after the trailer unit was moved from Oconto Falls. The results of these studies have been discussed separately in Sections V and VIII which deal with reverse osmosis design and engineering studies. The later data indicate that although velocities of 2.0 ft/sec may satisfy the theoretical requirements for adequate turbulence and mixing with NH_3-base wash water concentrations up to levels of 4.0 percent solids, the actual experimental evidence points to a need for minimum final velocities of 3.0 ft/sec at any point in the system to also satisfy the mass transfer requirements. Inlet velocities of not less than 2.7 ft/sec were employed in this NH_3-base demonstration program but the average and final velocities were substantially less than optimum at times and may have resulted in accumulative fouling affecting all banks of the trailer unit and especially in the final banks working at the higher levels of concentration.

Module Life Experience

Life performance for the original coat of 396 modules, with which the trailer was originally equipped in November 1968, proved to be about 7 to 8 months, as based upon experience at the end of the second demonstration. At the start of Demonstration No. 3, the failing mechanical strength of the membrane support tube apparently became a limiting factor. The evidence of module and tubular failures appeared to increase and to be critically dependent upon the operating pressures at 600 psig or higher. It would appear that stress and fatigue effects in the tubular support structures after six months of operation were responsible for the increasing number of module failures in the third demonstration at Oconto Falls. Later experience was pertinent during subsequent velocity-fouling studies conducted with the rebuilt modules over an 18-month period in the large-scale trailer unit at Appleton, when the module life was observed to be relatively much better at pressures of

400-500 psig. At times the unit was operated successfully with rebuilt modules at the lower pressures for as long as eight months without occurrence of any module failures.

Table 53 gives the history of module failures during the different period of trailer operation in this demonstration run at Oconto Falls. During the first period of June 9 to August 11, the trailer was operated for a total of 473 hours, during which some 62 out of 387 modules were removed and replaced due to leakage, usually following tube rupture. On August 11, 1969 fourteen tube ruptures occurred in 12 hours of actual operation. Decision to return all modules to the factory for rebuilding was made at that time and the unit was shut down August 12. The newly refurbished modules arrived back in Oconto Falls during the first week of October.

TABLE 53

HISTORY OF MODULE FAILURES

Period	Trailer Unit Operating Hours	Module Failures	
		Ruptured	Plugged & Leaked
June 9-July 18	0-171	6	1
July 19-25	172-273	12	0
July 26-August 11	274-472	37	6
August 11-October 1	- - - - - -Shut Down - - - - - -		
October 1-17	473-683	14	44

During the second and concluding period of the demonstration from October 7 to October 17, 1967, 211 hours of continuous operation were achieved with fourteen module failures due to tube rupture out of 238 modules. However, 44 of these new modules were removed and replaced due to leakage. Most of these leaks were found to be due to faulty sealing by the plastic sleeves which act as a gasket or seal in the tubular connections to the end caps and turnarounds. The failure of the plastic sleeves proved a major problem with the rebuilt modules.

Module life is understandably a very important factor in the economics of reverse osmosis systems. The membrane replacement costs for equipment marketed in 1970-71 account for as much as 40 percent of the total operating cost. Modules with a minimum life expectancy of 12 months, and preferably 18 to 24 months can be anticipated as a minimum requirement for economic feasibility in concentration processing of dilute pulp and paper effluents having little or no recovery of values to help support the operating charges.

Technical and Commercial Feasibility of Reverse Osmosis Concentration

The overall purpose of this field demonstration was to determine whether reverse osmosis can be feasibly developed as one of the alternatives for concentration processing of NH_3-base acid sulfite pulp wash water. This demonstration has provided us with the first available operating data from sustained runs on membrane processing of this type of pulp wash water. The second period of this large-scale demonstration along with special velocity-fouling studies described in Section VIII have helped to determine the required degrees of turbulence and mixing for maintaining sustained and practical levels of flux rates. No elaborate systems or procedures for pretreating the pulp wash water were required for this NH_3-base pulp wash water beyond normal adjustment of pH, temperature, and screening (100 mesh) to remove gross amounts of fiber and particulate matter.

The economics of reverse osmosis depends first upon recovering the effluents from the pulp mill in reasonably high concentrations to provide RO system feed liquors in sufficiently small volume to maintain low levels of capital charge for the membrane equipment. Secondly, the membrane module must have a minimum life expectancy of 12 months, and preferably 18 to 24 months.

The third important condition depends on maintaining permeation of clean water at economical flux rates. In this field trial the average feed concentration was 3 percent solids, which was considerably higher than the planned level of 1 percent dissolved solids. Average flux rates of 7 gfd were maintained in concentrating this pulp wash water within the range of 3 to 9 percent solids concentrations. For the purpose of engineering cost calculations, an overall flux of about 8 gfd might be expected in the range of 1 to 10 percent solids concentration, since 80 percent of the water is removed in the early stages of concentration below 5 percent solids. However, improvements in membrane performance from new types of equipment becoming available in 1971 can probably be counted upon to substantially improve the cost picture (Section X).

The ammonia-base acid sulfite mill at Oconto Falls, with a rated production of 120 tons per day, discharged a calculated average of 125,400 gallons per day of wash water, with a BOD load of 63 pounds per ton of product, and at 33 grams dissolved solids per liter (275 pounds per 1000 gallons) discharged about 38,533 pounds of spent liquor solids daily in this effluent. At 90 percent recovery of these solids in an overall concentration by reverse osmosis and by evaporation, some 17 tons of additional spent liquor solids might be recovered and marketed in the chemical sales division or alternately be burned for heat value. Utilization routes to disposal of the concentrate should substantially improve the economics of reverse osmosis in the prevailing, early commercialization stages of developing applications for RO in the pulp and paper industry.

The economics of reverse osmosis processing of this ammonia-base liquor, are the subject for detailed study in a comparative evaluation based on all five demonstrations as described in Section X and will not be discussed further in this chapter. However, the overall picture for the demonstration provides a substantial base for serious consideration of reverse osmosis as an effective and competitive route to concentration and recovery of heat or other values in the liquor solids and with elimination of one of the principal effluents contributing substantially to the total pollution load from this mill.

Supplementary Studies

The large-scale field demonstration at Oconto Falls was preceded by a substantial amount of laboratory and pilot scale field studies on various types of dilute wastes. The wastes included pulp wash water, evaporator condensate, and hypochlorite bleach effluent collected from various pulping and bleaching operations of the mill. It was concluded from these studies that the pulp wash water comprised a relatively large portion of the pollution load from the Oconto Falls mill and therefore the large-scale field demonstration was conducted on pulp wash water alone. During the initial pilot-scale field trials, a 9-week study was carried out to determine the feasibility for membrane concentration processing of a single-stage hypochlorite bleach effluent. It was the first of two field demonstrations on bleaching effluents and was carried out prior to Demonstration No. 4 on kraft bleach liquors at Cloquet, Minnesota. This supplementary section discusses the flux rate and rejection data obtained during this pilot-scale field study on hypochlorite bleach effluent.

Concentration Processing of Hypochlorite Bleach Effluent

The Oconto Falls mill discharged 3 million gallons of bleach effluent per day (equivalent to 25,000 gallons per ton of bleached pulp).

A typical analysis of this dilute bleach effluent follows:

Solids = 1.5 g/l
BOD$_5$ = 125 mg/l
COD = 500 mg/l
Calcium = 300 mg/l
Chlorine = 450 mg/l
Color = 100
Optical density at 281 nm = 2.1-2.5
pH = 6.7-8.2
Temperature = 12-27°C

The concentrations of the hypochlorite bleach effluent were substantially below what might be considered to be an economical level of concentration (5 to 10 grams per liter), but there was no practical way to obtain 500 to 1500 gallons daily of a more concentrated hypochlorite bleach effluent without substantial process modification and serious disruption of mill operations. This small pilot trial was, therefore, carried out on the available supply of very dilute bleach effluent with the use of Type 3 Calgon-Havens 18-tube modules manufactured in 1968. A number of continuous flux rate runs were made under conditions of both straight-through operation at low levels of concentration and also by a recycle run to achieve higher levels of concentration. The straight-through operations involved using nine modules set up in staged system with 2 parallel rows of 3 modules in series followed by one row of 3 modules in series. For recycling conditions, six modules were connected in two parallel rows.

These bleach effluent tests were conducted in the period from January 28 to March 6, 1969. During this time we had a total operating run of 807 hours.

Table 54 presents the data on the flux rates and operating variables. Table 54 indicates that the flux rates under straight-through conditions on a feed liquor having 1.0-1.6 grams per liter solids were low and leveled off at about 5.0 gfd at 600 psig and 35°C temperature. Under recycling conditions the flux rates dropped even further because of higher feed concentration. The concentrations during the recycling were increased by a factor of about six times and reached 9 grams per liter. The flux rate at this highest concentration was only 1.9 gfd at 35°C and 600 psig pressure.

Low flux rates were apparent and indicated serious fouling problems were being experienced at velocities of 2.9 ft/sec. Increasing the velocities to as high as 3.4 ft. per second did not improve the flux rate. One module was ball flushed at about 800 operating hours and the fouling material was analyzed. The fouling material contained 19.3 percent calcium and 37.4 percent ash. Therefore, it seems the membrane fouling was due to the accumulation of a mixture of calcium salts and organics on the membrane surface.

Subsequent experience indicated that this fouling might have been overcome by maintaining velocities higher than 4.0 ft/sec. However, in addition to the fouling problems, the high osmotic pressure of the liquor would be expected to adversely affect the starting flux rates. This is understandable because the osmotic pressure of a liquor increases rapidly in the presence of low molecular weight inorganic materials. This hypochlorite bleach effluent contained about 67 percent inorganics in the form of calcium chloride, and the organics represented only a small portion of the total material.

Table 55 gives the rejection data for hypochlorite bleach effluents. Percentage rejections for all components are fairly good as summarized below:

Solids	87-90
BOD_5	70-95
COD	85-99

TABLE 54

SUMMARY OF FLUX RATES AND OPERATING VARIABLES FOR HYPOCHLORITE BLEACH EFFLUENT

Operating Hours	Average Concentration of Feed, g/l	Average Pressure, psig (P)	Average Temperature, (T)	Average Inlet Velocity, ft/sec[b]	Average Flux Rate at P, psig and T°C gfd	Flux Rate Corrected to 600 psig and 35°C
Straight-Through: 2 Parallel Rows of 3 Modules[a] in Series Followed by 1 Row of 3 Modules in Series						
0-101	1.6	610.0	13.0	2.7	5.3	7.5
102-202	1.0	615.0	13.0	2.7	4.2	6.0
203-232	1.5	610.0	12.0	2.7	3.3	4.8
Recycle: Six 18-Tube Havens Modules - 2 Parallel Rows of 3 Modules in Series in Each Parallel Row						
233-348	3.6	580.0	23.0	3.4	2.5	3.3
349-508	4.5	570.0	26.0	3.4	2.2	2.8
509-556[c]	5.0	580.0	23.0	2.7	--	--
557-705	9.1	560.0	27.0	2.7	1.5	1.9
706-743	6.4	565.0	26.0	2.7	1.9	2.5
744-807[d]	6.0	570.0	24.0	2.7	3.1	4.0

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[a] Tap water flux rate = 20 at 35°C and 600 psig average pressure.

[b] This is average inlet velocity to Banks I/II. Average inlet velocity to Bank III varied 4.6-5.0 ft/sec depending on flux rate.

[c] The unit was down briefly due to module rupture in the 509-556 operating period.

[d] At 744 hours, the modules were ball flushed before the flux rate run.

Calcium	82-92
Chloride	80-90
Color	94-99

A rather remarkable phenomenon was observed with the reduced pH of the permeate. The pH of the permeate for the first sample was 2.7 units lower than the pH of feed and concentrate. The difference in pH became less with increasing operating time, and finally there was no difference at about 600 operating hours. This might indicate a slow buildup of fouling materials to provide a dynamically formed membrane with greater levels of rejection for components affecting the pH than that achieved by the cellulose acetate membrane alone.

TABLE 55

REJECTION DATA FOR HYPOCHLORITE BLEACH EFFLUENT

Sample No.	pH Feed	pH Concentrate	pH Permeate	Average Concentration of Feed, g/l	Rejection Ratio, percent Solids	BOD_5	COD	Calcium	Chloride	Optical Density at 281 nm	Color
					Straight-Through						
1	6.7	6.7	4.0	1.74	91.0	68.0	85.0	92.0	88.0	99.0	96.0
2	7.1	7.0	4.1	1.40	89.0	73.0	88.0	89.0	89.0	97.0	95.0
3	7.1	7.1	5.8	1.04	88.0	84.0	85.0	90.0	83.0	97.0	94.0
					Recycle						
4	7.2	7.1	6.2	1.49	87.0	77.0	87.0	82.0	77.0	99.0	95.0
5	7.3	7.2	6.7	1.28	86.0	78.0	86.0	84.0	83.0	98.0	92.0
6	7.6	7.7	7.1	3.56	85.0	83.0	95.0	86.0	79.0	99.0	99.0
7	8.2	8.2	7.5	4.51	85.0	93.0	96.0	91.0	77.0	98.0	98.0
8	7.6	7.6	7.6	9.28	88.0	95.0	99.0	89.0	81.0	99.0	99.0
9	7.4	7.4	7.2	8.86	89.0	97.0	99.0	88.0	82.0	99.0	99.0
10	7.0	7.0	6.6	4.86	87.0	88.0	97.0	87.0	82.0	98.0	94.0
11	7.7	7.7	7.3	7.19	91.0	91.0	98.0	89.0	87.0	99.0	98.0

It can be concluded that membrane fouling was a serious problem during these bleach effluent studies, and any further investigation of the treatment of hypochlorite bleach effluent which might be undertaken with use of RO should be aimed at finding methods for reducing the degree of fouling. One of the methods worth considering is to maintain higher degrees of turbulence and mixing across the membrane surface. Another possible route may be the employment of pretreatment steps for the bleach effluent feed ahead of the membrane system. Lime and ferric treatment, addition of polyelectrolytes, coagulation, and filtration are examples of such pretreatments which might be considered.

CONCLUSIONS

This field demonstration of reverse osmosis concentration processing of ammonia-base acid sulfite pulp wash water operated at flow rates on the order of 50,000 gallons per day. The trailer was operated for a total of 683 hours, during which about 1.2 million gallons of liquor were processed to produce 400,000 gal. of 10 percent TS concentrate and 800,000 gallons of clean reusable water.

Serious problems of membrane module failure were encountered throughout this field trial.

Average flux rates of 7 gallons per square foot per day were maintained in concentrating the pulp wash water in the range of 3 to 9 percent solids concentrations. For the purpose of engineering cost calculations, an overall flux rate of at least 8 gallons per square foot per day might be expected with use of membrane equipment available in 1968-70 to achieve a concentration in the range of 1 to 10 percent solids, as based upon 80 percent of the water being removed in early stages of concentration below 5 percent solids.

No elaborate or expensive pretreatment of pulp wash water was required beyond nominal amounts of temperature adjustment, pH control, and suspended solids removal through a 100-mesh screen.

The pulp wash waters processed in this third demonstration contained relatively small amounts of colloidal and particulate matter. These amounts were not shown to be of concern in these trials, since we were able to control the fouling of the membrane surfaces by maintaining moderate levels of velocity of flow. Velocity of flow at higher levels of concentration was indicated to be an important means of maintaining high overall rates of flux, however. RO processing of Ca hypochlorite bleach effluent did not appear promising under the conditions of processing the very dilute feed liquor available for the test runs undertaken.

FIELD DEMONSTRATION NO. 4

CONCENTRATION PROCESSING OF CAUSTIC EXTRACTION KRAFT BLEACH EFFLUENT BY REVERSE OSMOSIS

This section describes laboratory and field studies conducted as Demonstration No. 4 in the series conducted under Federal Research and Demonstration Grant 12040 EEL to the Effluent Processes Group at The Institute of Paper Chemistry. The demonstration field trial was conducted at the Cloquet, Minnesota kraft pulp mill of The Northwest Paper Company Division of Potlatch Forests as a feasibility study for concentration processing of alkali extraction kraft bleach plant effluent (alkali extraction KBE).

This demonstration was preceded by a substantial amount of laboratory and small-scale pilot study on various types of bleach plant effluents from various mills and various types and sequences of bleaching operations. (See Section V.) It has been concluded that the alkaline extraction KBE and particularly the second-stage effluent in bleach sequences such as CEDED comprises one of the more serious pollution problems from kraft mill bleach plants. A large part of the pollution loading from bleaching operations from the Cloquet mill derives from this source (secondary alkali extraction KBE). As such, it has been of particular interest to develop new methods for treating this type of bleach waste as alternatives to conventional disposal routes, such as by bio-oxidation.

Problems were recognized in undertaking these studies. High levels of dilution have been of particular concern. The Cloquet kraft mill was designed to produce fine quality grades of bleached kraft paper by the best methods prevailing at the time of its construction. Accepted good bleaching practice at that time called for using large amounts of water for washing the pulp. The bleach plant effluent which could be made available at this mill was, therefore, representative of the very dilute wash water characteristic of this type of bleach washing operation. These large volumes of bleach effluents, with low concentrations of dissolved solids, are more dilute than would be desirable for a commercial RO operation for concentrating and disposing of the bleach plant effluent.

More modern bleach plant design and bleaching practices are proving that large volumes of total bleach plant wash waters can be substantially reduced from the prevailing levels of 10,000 to 50,000 gallons per ton of bleached pulp to volumes as low as 6000 gallons per ton. With this in mind, planning proceeded for a field demonstration trial of reverse osmosis processing of the alkaline extraction KBE, which is presently available in volumes estimated to be on the order of 7000 gal./ton pulp within the total volume of all bleach effluents at this mill. The objective was to be directed to concentrating this dilute effluent having less than 1 percent solids to an intermediate stage concentrate at around 10 percent solids content in one-tenth or less of the original volume. It could then be expected that the 10 percent solids concentrate could be feasibly processed for final disposal or utilization to achieve much more complete pollution control than by bio-oxidation of the dilute flows. Methods for final processing of the 10 percent solids concentrate of bleach liquors are known to be developing as a new phase of research on bleach plant effluents and could feasibly include further concentration of the 10 percent solids product to 50 percent or higher for combustion or other suitable methods of final disposal.

NATURE OF BLEACH PLANT TREATMENT PROBLEMS

Bleach plant effluents from pulp mills represent a significant pollution loading on receiving waters. Suspended fiber in these effluents first requires clarification treatment. Dissolved solids may range to several hundred pounds per ton of bleached pulp and the BOD_5 from 10 to 50 pounds per ton. Special problems are apparent in respect to color, foaming, content of resistant organics, inorganic salts, and also components toxic to fish may be present.

Kraft mills, especially those in mild climates, may employ conventional primary clarification and secondary bio-oxidation techniques to treat dilute bleach wastes for removal of suspended solids and BOD_5. Problems may arise if more complete treatment is required. A 1968 survey[12] showed that 82 out of a total of 112 mills with combined kraft mill effluents provided primary treatment, and 55 provided some form of secondary treatment, such as storage oxidation basins, aerated stabilization basins, or activated sludge.

Biological oxidation does not significantly reduce the color of these effluents. It is known that lime precipitation treatment will substantially reduce the refractory organic colored components[13]. The massive lime process which has been developed through larger scale pilot planting is presently being tried commercially[14]. Recently, work on coagulation[15,16] has shown that Al^{+3} and Fe^{+3} can be used to reduce the color of both chlorination stage and caustic extraction bleach wastes. As much as 96.5 percent of the color and 85 percent of the total organic carbon are removed under optimum conditions from the alkaline extraction KBE. However, settling and dewatering of the resultant floc has been shown to be a problem.

Fuchs[17] has shown that activated carbon can be effective in reduction of the color in caustic extraction KBE. This may account for 60-80 percent of the color in the total of all KBE streams.

One important objective in treating bleach effluents is to recover clear water for reuse, and particularly for recycle to final wash stages. For this there is need to know more about the quality of water required for use in bleaching and pulp washing. Smith and Berger[18] have studied one route to this end. They show that reusable process water from total unbleached kraft mill effluents could be obtained by a process comprised of primary clarification of suspended solids, massive lime precipitation for color reduction, bio-oxidation to reduce BOD, and a final treatment with activated carbon. This four-step processing was estimated to cost 14.5¢/1000 gallons. The addition of ion exchange demineralization might add 25¢/1000 gallons in the case of alkaline extraction KBE, but removal of chlorides from total bleach effluents remains as a substantial problem. The degree of recycle of NaCl which can be tolerated in a bleach system may be fairly high in some situations, less in others.

Water quality necessary in the production of bleached and unbleached kraft pulp as compiled by Berger[19] is given in Table 56.

TABLE 56

RANGES OF DESIRED PROPERTIES OF PROCESS WATER FOR KRAFT PULPING AND BLEACHING OPERATIONS

	Unbleached	Bleached
Turbidity, units	5-25	0-5
Color units	10-80	0-5
pH	6.5-8.0	6.8-7.3
Total alkalinity, mg/l	20-150	20-75
Hardness, (as $CaCO_3$), mg/l	5-200	5-100
Dissolved solids, mg/l	50-500	50-250
Chloride, mg/l	10-150	10-150
Iron, mg/l	0.5 max.	0.2 max.
Manganese, mg/l	0.3 max.	0.1 max.
COD, mg/l	0-12	0-8
BOD_5, mg/l	0-5	0-2

A large proportion of the existing bleach plant operations employ large volumes of water with effluent volumes ranging from 20,000 to 40,000 gallons per ton of product. Under these conditions, research and development objectives as well as practical installations have understandably been directed to appropriate disposal or reuse methods of treatment based on handling such large volumes of relatively weak effluents.

A variety of methods are being developed to accomplish volume reduction. Continuous bleaching systems are a principal route in new plants. Existing bleach plants may be modified to various degrees for countercurrent washing, for diffusion washing[20], for extracting and pressing of high consistency pulps, and by innovating in various other ways. Indications are that a higher concentration may be obtained in most mills as an incentive for changing the bleach system in coming years. It becomes reasonable to consider new, alternative methods for more complete treatment of bleach wastes where low volumes of flow in the range of 7000 gallons per ton of pulp are available[21]. Recovery and reuse of bleach chemicals as well as recovery and recycle of reusable water can be brought into focus as additional objectives for overall bleach effluent treatment with availability of concentrates at 10 percent solids or higher. Spent bleaching chemicals in the form of 200 to 300 pounds of sodium chloride per ton of bleached pulp could lead to recovery of as much as 50 tons of NaCl per day in a 500-ton bleach plant.

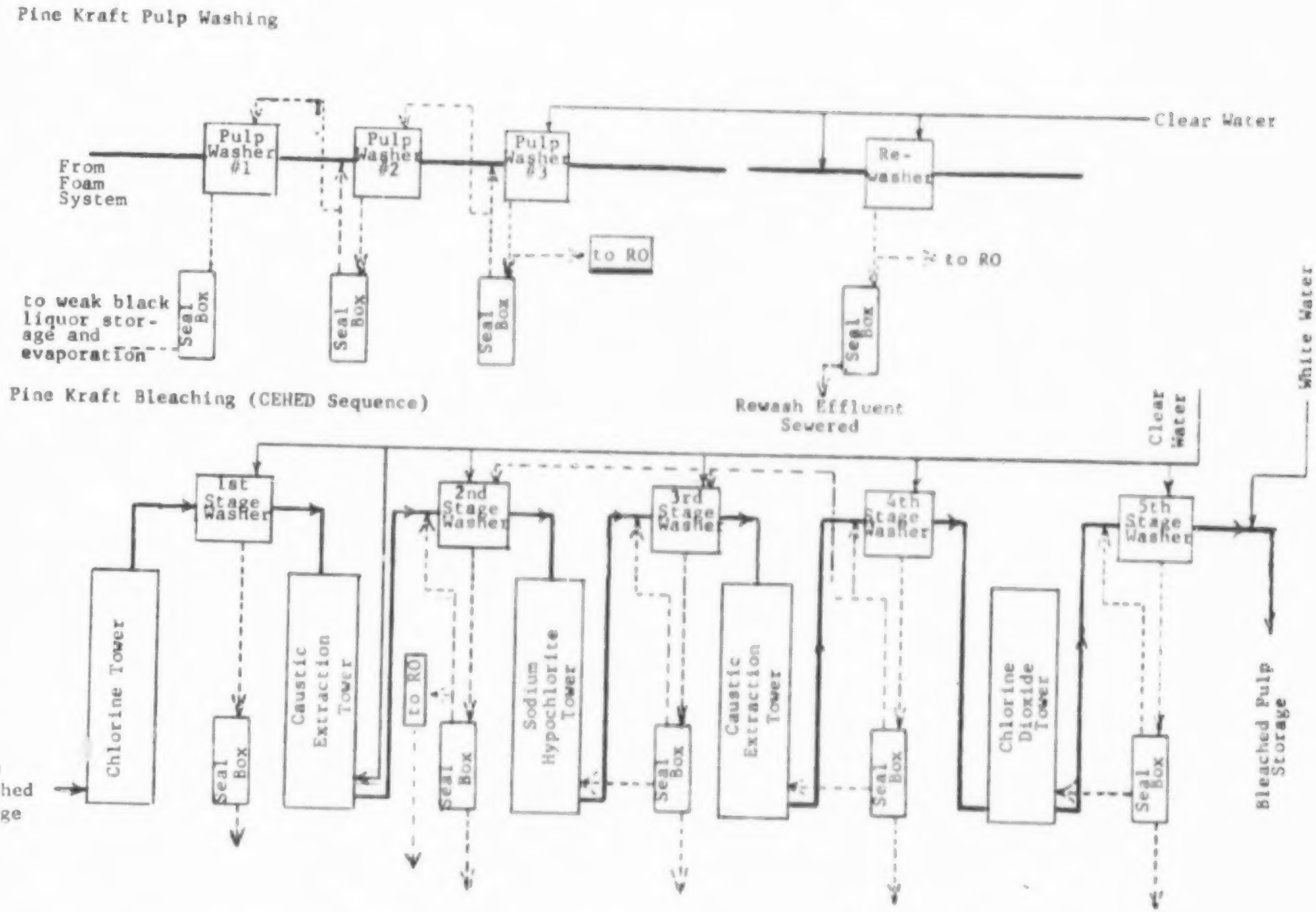
CHARACTERIZATION OF KRAFT BLEACH EFFLUENT AT CLOQUET

The studies in this demonstration trial of reverse osmosis were carried out on alkaline extraction KBE from kraft pulping of pinewood. The mill is rated at 185 tons daily of softwood kraft pulp and 120 tons of hardwood kraft pulp.

Figure 30 provides a flow sheet for the kraft pulp washing and bleaching of the pine softwood pulps. Some special studies for concentration processing of the rewash water from the pine pulp mill are reported in a final section of this report, but this section is primarily concerned with the alkaline extraction KBE from the second stage in the bleaching sequence. Dilute liquor from the seal box from the second-stage washer was piped at about 0.25 percent solids concentration to the reverse osmosis pilot unit installed at this mill, see photo, Fig. 65 (Appendix B). Similar effluent was collected and sent to Appleton for laboratory studies conducted before, during, and after the pilot runs in Field Demonstration No. 4.

For the demonstration run, about 1500 gallons of caustic extraction effluent were processed daily by reverse osmosis. The mill staff calculated that about 30,000 gallons of total bleach plant effluent were derived from each ton of bleach pulp production, and that the alkaline KBE accounted for about 7000 gallons of this total effluent from each ton of pulp production.

Table 57 provides average analytical data from 13 samples of the dilute feed liquor collected during these field and laboratory studies on membrane processing of the kraft extraction bleach plant effluent for Demonstration No. 4. The dilution of this bleach plant effluent was much greater than desired, but represented the best concentration obtainable at this mill at the time of these studies. Solids concentration at 2.6 grams per liter is about one-fourth of the desired 1 percent level which might be considered economically feasible for commercial operation. The BOD_5 and COD of this liquor were fairly high at 190 and 1410 mg/l, respectively. Color is also a characteristic of concern


Pine Kraft Pulp Washing

Pine Kraft Bleaching (CEHED Sequence)

From Foam System
Pulp Washer #1
Pulp Washer #2
Pulp Washer #3
Re-washer
Clear Water
to RO
to RO
Seal Box
Seal Box
Seal Box
Seal Box
to weak black liquor storage and evaporation
Rewash Effluent Sewered
from unbleached storage
Chlorine Tower
1st Stage Washer
Seal Box
Caustic Extraction Tower
to RO
2nd Stage Washer
Seal Box
Sodium Hypochlorite Tower
3rd Stage Washer
Seal Box
Caustic Extraction Tower
4th Stage Washer
Seal Box
Chlorine Dioxide Tower
5th Stage Washer
Seal Box
Clear Water
White Water
Bleached Pulp Storage

Figure 30. Kraft Mill Pulp Washing and Bleaching Schematic

in pollution control. Much of the color deriving from the entire bleaching operation can be found in the caustic extraction effluent.

TABLE 57

RO KRAFT CAUSTIC EXTRACTION KBE FEED CONCENTRATIONS

Solids	2630 mg/l
BOD$_5$	190 mg/l
COD	1410 mg/l
Optical density, 281 nm	18.2
Sodium	6.0 mg/l
Chlorides	490 mg/l
Color	6000

Table 58 provides additional analytical information showing the variation in analysis for samples obtained from Stage 1 (chlorination) and Stage 2 (caustic extraction) for a variety of types and kinds of bleach liquors, as well as kraft softwood caustic extract. The differences were especially dependent upon the degree of dilution characteristic of each different pulp mill and of the different types of pulp and stages of bleaching. The purpose in presenting Table 58 is to help in showing the importance of having a good analytical characterization of the particular type of liquor to be studied in any individual mill operation, and to place the results of the studies reported for this demonstration in proper perspective.

The dilution of the liquor available for feeding to the reverse osmosis system in these studies presented no technical problems. RO concentration by factors as high as 60 times could be demonstrated in these studies. Dilution is an economic problem in terms of capital cost and operating charges for concentration systems. Economic feasibility of any commercial operation to be undertaken at this mill would be substantially improved if the feed liquor were reduced to about one-fourth of its volume and then to employ a concentration factor of perhaps 15 times for the membrane processing step. This point will be discussed in greater detail in the concluding section of this report.

TABLE 58

VARIATION IN ANALYTICAL CHARACTERISTICS
OF DIFFERENT BLEACH LIQUORS

		Solids		BOD_5		pH	Temp.,
		mg/l	lb/ton	mg/l	lb/ton	Approx.	°C
STAGE 1 (Chlorination)							
Hardwood	Hi	869	43	169	20	2	21
Kraft	Low			141	8.3		
Softwood	Hi	11,600	214	294	25	2.1	21
Kraft	Low	594	67	102	6		
Hardwood	Hi	1,180	245	159	24.9	2.2	
Sulfite	Low	1,000	149	102	20.1	1.96	
Softwood	Hi	2,280	321	331	25.1	2.52	
Sulfite	Low	640	94	38	7.6	1.82	
STAGE 2 (Caustic Extraction)							
Hardwood	Hi	1,750	83	179	14	10	65.5
Kraft	Low			125	6	10	
Softwood	Hi	5,980	223	877	12.2	9.9	65.5
Kraft	Low	1,800	40	46	5.7		
Hardwood	Hi	4,020	835	575	117.4	7.54	
Sulfite	Low	1,390	207	196	29.6	6.72	
Softwood	Hi	2,780	391	420	59.1	7.73	
Sulfite	Low	490	70	25	5.4	6.65	

THE EXPERIMENTAL PROGRAM

Laboratory Phases

A great deal of laboratory work in the central laboratory of the Effluent Processes Group at The Institute of Paper Chemistry was conducted prior to undertaking the field demonstration run with equipment installed at Cloquet. Laboratory studies were also conducted concurrently with the field run in Cloquet and also in confirming studies after that run was completed. These laboratory studies were directed first to establishing the degree of pretreatment needed for successful operation of the reverse osmosis equipment. The findings were similar to those in the previous demonstrations:

Gross amounts of fiber were removed by 40 to 100 mesh screening ahead of the membrane system.

Adjustment of pH may be necessary to have the feed liquor within the safe operating range of pH 3.0 to 7.0 for cellulose acetate membranes. Several sources of acid were evaluated in the laboratory studies for neutralizing the alkaline extract. For Demonstration No. 4 sulfuric acid was used to neutralize to a pH of about 7.0 ± 0.2. There is still some question as to the exact level of pH adjustment which may actually be needed in commercial operation. Manufacturers of reverse osmosis equipment using cellulose acetate membranes normally specify a range between 4.0 and 7.0, but in some cases pH levels substantially above and below this range apparently have been tolerated without evidence of membrane hydrolysis. A pH of 7.0 seemed to be entirely satisfactory for all studies conducted under this demonstration on caustic extraction KBE. A technical-grade sulfuric acid was used for the purpose of maintaining reliable and close control in these studies, but it was also demonstrated that other sources of acid, such as the chlorination stage KBE, could be used satisfactorily to achieve the same purpose and at much lower cost.

Temperature adjustment was not required for processing the bleach plant effluents in this particular study, although some bleach effluents have a relatively high temperature and might require cooling below about 40°C to avoid damage to the membranes. On the other hand, some effluents are too cool for obtaining good flux rates and might advantageously be warmed to above 25°C. Average operations for Demonstration No. 4 were carried out at a temperature range of 30 to 35°C.

Fouling problems have always been a matter of concern in developing procedures for processing each new type of waste flow. No need was found for other pretreatment steps ahead of the reverse osmosis system. However, careful evaluation was made of possible need for preventing fouling of the membrane during these studies. No serious problems resulted after the initial laboratory work developed operating parameters to avoid fouling. At lower velocities and degrees of turbulence, it was found advantageous to practice the pulsing procedure of operating the system under periodic release of the membrane system from high pressure for periods of 30 seconds to several minutes every hour or so. Later experience would seem to indicate that if the velocity of flow is greater than the levels required to prevent concentration polarization, the need for the so-called pulsing operation may be greatly reduced. However, the periodic pressure reductions still seem to have advantage when carried out on a daily basis, and may be related to membrane compaction as well as to concentration polarization and actual fouling of the membranes.

Fouling, as such, did not appear to be a problem in this field demonstration. Fouling can occur to different degrees with different types of pulping and bleaching liquors. Where fermentable materials, such as wood sugars, are present in the spent liquor, steps should be taken to prevent microbiological sliming of the membranes. Sliming may occur rapidly during shutdown periods of a day or more if liquor stands in contact with the membranes; whereas continuous operation at sufficiently high velocities may keep the membranes clean indefinitely. No problems were experienced with membrane fouling during continuous operation in this field trial.

Pilot-Plant Field Study

A substantial amount of experience with operating conditions at the Cloquet mill of The Northwest Paper Company had been gained in an earlier study on concentrating kraft pulping rewash waters during the summer months of 1968. The mill staff subsequently determined that planned changes in the pulping process would eventually eliminate the rewash waters as a waste flow from this mill. Plans for Demonstration No. 4 were, therefore, changed to develop methods for concentration processing of the caustic extraction KBE For this modified demonstration preliminary data and experience were needed with one of the smaller pilot-scale field units operating at the 1500 gal./day level. It was further decided to develop all data from this trial with the small unit. Scale-up data were available from the first three demonstrations using both the small and large 50,000 gal./day field units. Long delays were being experienced in obtaining reliable and properly tested membrane modules then being produced in early stages of commercial production by the several equipment suppliers active in this new field of membrane processing. It was not yet possible to justify the large capital expenditure necessary for replacing the early prototype modules with which the large field unit had been equipped for Demonstrations 1, 2, and 3.

Under these circumstances, it was agreed to employ one of the smaller pilot scale Milton-Roy Duplex pumping units with capacity up to 6 gallons per minute, together with a membrane unit containing 20 modules of the Type 3 configuration available from the larger trailer unit. Later in the run a bank of five Type 3 modules of the mid-1970 design were installed. This unit was placed on stream at Cloquet, Minnesota effective September 15, 1970 and ran through December 15, 1970.

Description of Equipment and Pretreatment Procedure

The equipment for pretreatment and the reverse osmosis equipment were substantially the same for each of the three phases of the overall study. The second-stage washer effluent from the rotary vacuum washer was taken directly from the recycle loop at the washer seal box, and was piped approximately 50 feet through flexible plastic hose to a 100-mesh nylon side hill screen. The screened bleach plant effluent passed through to a 110-gallon stainless steel mix tank where dilute sulfuric acid was added under automatic control to adjust the pH to 7.0. A relatively constant temperature was maintained by means of a cooling coil in the mix tank. The pretreated liquor was then pumped to a 50-gallon polyethylene holding tank from which it flowed by equalized level to two 50-gallon plastic feed tanks. These two feed tanks made it possible to service two separate pressurized reverse osmosis systems set up in either series or in parallel configuration. The Milton Roy main pressurizing pump was a duplex unit with each of the two pumps having an adjustable stroke length rated from zero to slightly less than three gallons per minute and up to 1100 psi. Draw-off of the concentrate from the final feed tanks was accomplished by means of a Brosites metering pump. The permeate was allowed to flow to the sewer after sampling. A flow diagram for the system is shown in Fig. 31.

DATA AND RESULTS

It was not possible to accomplish complete, straight-through concentration from 1 to 10 percent dissolved solids with the small-scale equipment because of the limitation on the number of stages that could be studied with a limited number of modules and with no more than two pumping stages. The program for the 3-month study was, therefore, divided into three stages of concentration. Phase I, for the period September 21 through October 8, was a dilute phase study starting with bleach effluent having a feed concentration of only 2 to 3 grams per liter as received from the mill. This was concentrated to about half the original volume and to a dissolved solids level ranging between 4 and 5 grams per liter. The second phase provided one month of study for concentrating in the range of about 1 percent solids to upwards of 5 percent solids. The third phase carried the concentration on up to as high as 15 percent solids (160 grams per liter). An outline of the planned operating conditions for these three phases of study is provided in Table 59, and more detailed operating data are provided and described later in Tables 62, 63, and 64.

Phase I — Data and Results

Two parallel systems were set up each with five modules in series under Banks A and B. Initially, Bank A was fed at a velocity of about 2.5 feet per second, while Bank B was fed at a lower velocity of about 1.7 feet per second. A steady state for the flux rate was established after about eight days of nearly continuous operation. The flux rates were fairly high in the first days but subsequently dropped substantially over 8 days of operation due to the low feed velocities.

Low levels of concentration were achieved in the range of 3 to 3.5 grams per liter in the concentrate. Rejections were quite good in

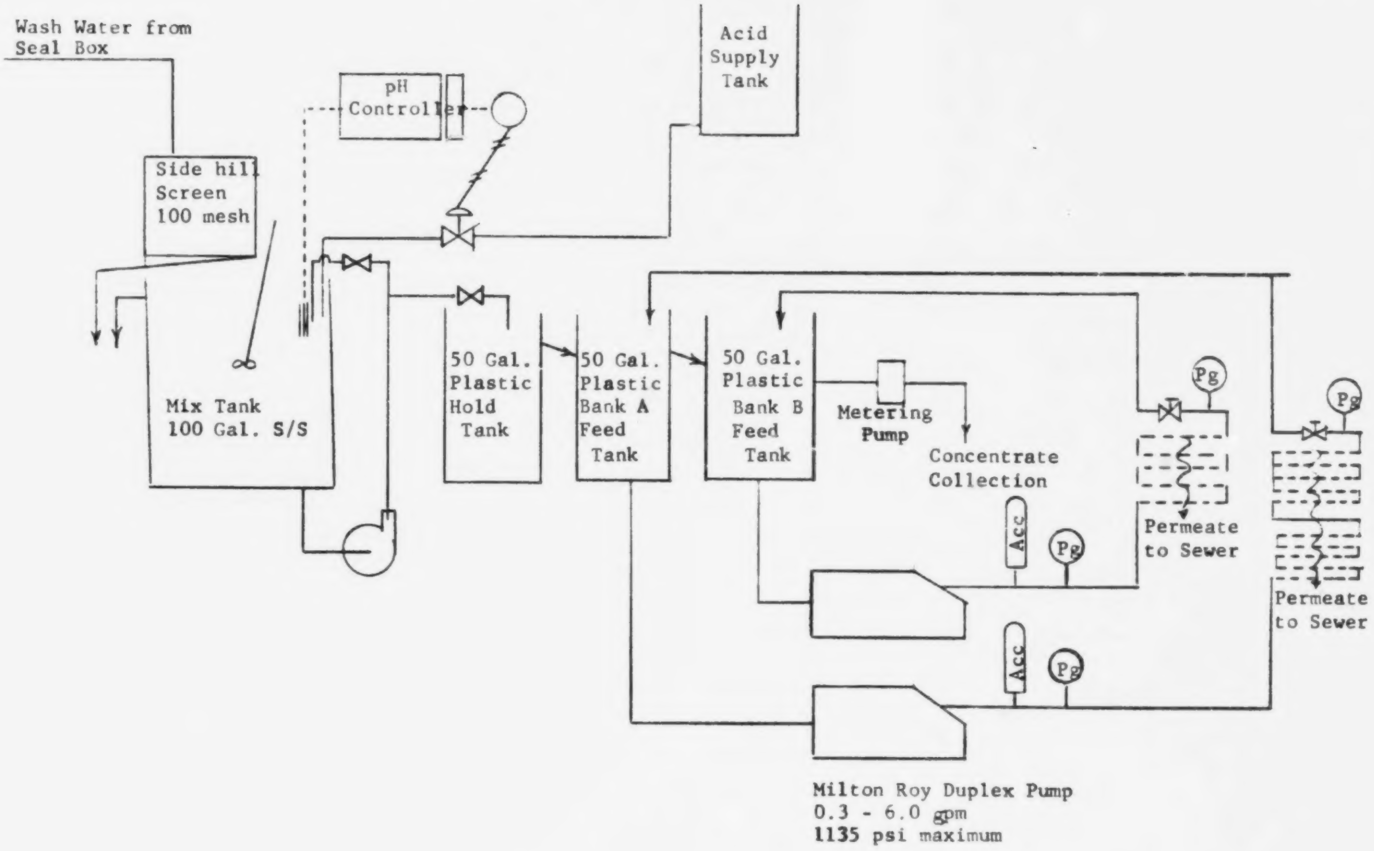

Wash Water from
Seal Box
Side hill
Screen
100 mesh
pH
Controller
Acid
Supply
Tank
Mix Tank
100 Gal. S/S
50 Gal.
Plastic
Hold
Tank
50 Gal.
Plastic
Bank A
Feed
Tank
50 Gal.
Plastic
Bank B
Feed
Tank
Metering
Pump
Concentrate
Collection
Pg
Acc
Pg
Acc
Pg
Pg
Permeate
to Sewer
Permeate
to Sewer
Milton Roy Duplex Pump
0.3 - 6.0 gpm
1135 psi maximum

Figure 31. Flowsheet-RO Processing of Alkaline Extraction KBE

TABLE 59

OUTLINE OF OPERATING CONDITIONS
RO PROCESSING OF ALKALINE EXTRACTION KBE

Date	Module Bank	Stage	Recycle	Solids Concentrate g/l		Vel., ft/sec		Pressure, psig		Number and Type of Series Modules
						In	Out	In(max)	ΔP	
Phase I				In	Out					
9/21 to 9/29	A	1	No	2	3	2.6	1.7	515	35	5 "used"[a]
	B	1	No	2	5	1.6	0.7	500	35	5 "used"
10/1 to 10/13	A	1	No	3	4	4.2	3.7	555	160	5 "used"
	B	1	No	3	4	3.2	2.5	520	55	5 "used"
Phase II										
10/14 to 10/22	A	1	Yes	2.5	40	3.2	2.5	525	85	5 "used"
	B	1	Yes	2.5	35	4.2	3.9	520	100	5 "used"
10/22 to 11/5	B	1	Yes	2.5	6	4.2	3.9	590	185	5 "used"
	A	2	Yes	5	82	4.2	4.0	475	100	5 "used
Phase III										
11/5 to 12/3	B	1	Yes	2.5	22	3.2	2.5	520	130	10 "used"
	A	2	Yes	7	130	4.2	3.7	810	230	5 new[b]
12/3 to 12/16	B	1	Yes	2.5	20	2.2	1.2	515	30	9 "used"
	A	2	Yes	7	160	3.2	2.7	795	155	5 new

[a] "Used" modules were Type 3 modules which had seen prior use both at previous demonstration site for pilot studies, and were prone to seal leaks or a tube rupture at pressures over 500 psig.

[b] New modules are Type 3 incorporating redesigned heads and turn arounds and rated for service at 800 psig.

the range of 90 percent or higher for most components, except BOD_5, which was about 76 percent rejected in the first week.

In the second week the feed rates were raised to correspond to inlet velocities of 4.2 and 3.2 ft/sec. The rate and extent of the flux rate decline decreased so as to give steady state flux rates of 9.1 and 9.0 gfd, respectively, when adjusted to 600 psig and 35°C.

Problems with module seal leakage became more serious as the inlet pressures were increased to give the same average system pressure (485 psig) at the higher velocities. Problems with leaky modules were apparent in the form of temporary development of a substantial amount of color in the permeate when the average system pressure exceeded about 500 pounds per square inch in these old modules. A shutdown for a short period of 5 minutes resulted in closure of the leaky seals in the heads of the modules a few minutes after operation was resumed.

Studies during the first month of operation confirmed the importance of maintaining initial feed velocities to the modules above 2 feet per second. A characteristic fall-off in flux rates occurred at lower levels of velocity, but the flux rates rose substantially again when the velocities were increased to 3.2 and 4.2 feet per second for Banks A and B in the later stages of Phase I. Comparison of steady state flux rates obtained at various velocities of flow in the module are shown in Table 60.

TABLE 60

STEADY STATE FLUX RATES OF
ALKALINE EXTRACTION KBE

(Without pressure pulsing)

Average Velocity, ft/sec	Product Water Flux Rate at 485 psig and 35°C, gfd
1.1	3.8
2.1	4.8
2.8	7.1
3.9	7.2
Initial	11

Table 61 presents data summarizing the average rejections for the dilute feed as determined from nine samples taken during straight-through operation. It was apparent that a substantial part of the dissolved solids were of low molecular weight, since it is normal to expect the rejection of dissolved solids of pulp wash waters to exceed 90 percent and usually better than 95 percent. Two low readings, apparently caused by seal leakage, indicated by [a] and [b], significantly affect the high average rejection of color and optical density.

TABLE 61

AVERAGE REJECTIONS OF PHASE I (STRAIGHT-THROUGH PROCESSING) (PERCENT)
ALKALINE EXTRACTION KBE

Constituent	Rejection, percent (1-Cp/Cc)100, av of 9
Total solids	85.4
BOD_5	74.2
COD	93.4
Optical density at 281 nm	97.7[a]
Sodium	77.3
Chlorides	64.9
Color	97.9[b]

---

[a] Seven determinations of nine ranged 98.5 to 99.2 percent.

[b] Seven determinations of nine ranged 99.6 to 99.9 percent.

Detailed presentation of data accumulated in Phase I are shown in Table 62. These data are significant in terms of showing no technical problems or roadblocks to membrane process concentration of very dilute bleach effluents. The problems to be faced in processing such dilute waters are economic in nature, and are associated with the expense of removing large quantities of water to achieve significant levels of concentration of the dissolved materials. It would be better to use the bulk of these dilute effluents as early stage wash waters in countercurrent or diffusion washing systems prior to membrane concentration.

Description of Phase II Operation

These studies were continued with the same equipment at higher concentrations in Phase II, as shown in Table 63. However, in Phase II the concentrate was recycled back to the feed tank in order to reach and

TABLE 62

PHASE I - PERFORMANCE DATA
STRAIGHT THROUGH RO PROCESSING OF KBE

	9/22/70		9/24/70		9/29/70		10/8/70	
	Bank A	**Bank B**	**Bank A**	**Bank B**	**Bank A**	**Bank B**	**Bank A**	**Bank B**
Solids, mg/l					-No Samples - Leaking Modules in Bank A-			
Feed	2044		1984		2884		3120	
Concentrate	2892	3648	3004	4628		3460	3512	3840
Permeate	134	227	155	258		635	637	383
Rej., percent	93.4	88.9	92.2	87.0		78.0	79.6	87.7
BOD, mg/l								
Feed	170		140		194		181	
Concentrate	174	212	208	278		267	--	182
Permeate	40	40	44	46		59	51	46
Rej., percent	76.5	76.5	68.6	67.1		69.6	71.8	74.6
COD, mg/l								
Feed	1208		1308		1596		1504	
Concentrate	1658	2082	1912	2942		1996	1734	1888
Permeate	60	64	78	84		95	88	79
Rej., percent	94.0	94.7	94	93.6		94.0	94.1	94.7
Sodium, mg/l								
Feed	472		460		632		720	
Concentrate	630	785	635	915		790	835	890
Permeate	50	86	55	102		224	242	134
Rej., percent	89.4	81.8	88.0	77.8		64.6	66.4	81.4
Color								
Feed	6000		5000		7000		7000	
Concentrate	8750	10,000	7500	13,750		7500	7500	8750
Permeate	7	7	20	10		30	25	15
Rej., percent	99.9	99.9	99.6	99.8		99.6	99.6	99.9
OD @ 281 nm								
Feed	13.92		14.56		20.64		18.8	
Concentrate	20.2	26.2	21.4	35.4		26.95	21.5	24.0
Permeate	.110	.126	.130	.129		.30	.225	.140
Rej., percent	99.2	99.1	99.1	99.1		98.5	98.8	99.2
pH								
Feed	6.59		6.65		7.03		7.00	
Concentrate	6.78	6.88	6.82	6.92		7.05	7.16	7.23
Permeate	5.81	5.90	5.80	5.80		7.10	6.70	6.49
Resistance ohm-cm @ 25°C								
Feed	481		457		344		291	
Concentrate	343	282	329	223		295	--	196
Permeate	4028	2685	3433	2042		864	813	1420
Temp., °C	36	36	33	33		33.5	31	31
Pressure, psig (in/out)	500/465	500/465	515/480	490/460		510/440	555/395	520/465
Permeate, ml/min	385	369	393	425		165	284	347
Velocity, ft/sec	2.6	1.6	2.6	1.6		1.6	4.2	3.2
gfd/485 psig @ 36°C	8.65	8.15	9.0	11.4		3.88	7.7	8.5
gfd/600 psig @ 35°C	10.7	10.3	11.1	12.8		4.9	8.9	10.3

TABLE 63

PERFORMANCE DATA SUMMARY - PHASES I AND II

	Phase I		Phase II			
	10/13/70		10/15/70		10/20/70	
	Bank A	Bank B	Bank A	Bank B	Bank A	Bank B
Solids, mg/l						
Feed	2870		12,630	16,070	35,230	41,310
Concentrate	3146	3276	17,170	17,450	31,130	48,000
Permeate	611	486	1533	1252	1494	1051
Rej., percent	87.9	83.1	87.9	92.2	95.8	97.4
BOD, mg/l						
Feed	125		553	852	1530	1605
Concentrate	117	118	1255	1255	1230	1855
Permeate	22	24	166	181	74	52
Rej., percent	82.4	80.8	70.0	78.8	95.2	96.8
COD, mg/l						
Feed	1332		7530	9430	27,300	27,260
Concentrate	1450	1450	10,590	10,050	24,580	31,020
Permeate	116	144	193	142	221	126
Rej., percent	91.3	89.2	97.4	98.5	99.2	99.5
Sodium, mg/l						
Feed	696		2840	3560	5920	7760
Concentrate	795	820	3900	4000	5500	8800
Permeate	207	163	534	461	486	364
Rej., percent	70.2	76.6	81.2	87.0	91.8	95.3
Color						
Feed	4000		32,000	40.000	150,000	130,000
Concentrate	6250	6250	50,000	45,000	137,500	150,000
Permeate	300	400	100	500	200	600
Rej., percent	92.5	90.0	99.7	99.9	99.9	99.9
OD @ 281 nm						
Feed	16.2		93.6	115.6	364	360
Concentrate	18.0	18.2	135.0	125.5	322.5	400
Permeate	0.87	1.31	1.10	0.585	1.595	0.631
Rej., percent	94.6	91.9	98.8	99.5	99.6	99.8
pH						
Feed	6.93		7.14	7.29	7.3	7.39
Concentrate	7.18	7.09	7.28	7.39	7.32	7.40
Permeate	6.72	6.70	6.83	7.19	7.49	7.14
Resistance ohm-cm @ 25°C						
Feed	313		105	84	61	45
Concentrate	291	276	85	78	66	42
Permeate	918	1260	396	454	245	553
Temp., °C	30	30	31	32	31	33
Pressure, psig (in/out)	535/380	520/420	520/445	465/370	525/440	520/420
Permeate, ml/min	256	232	224	202	178	173
Velocity, ft/sec	4.2	3.2	3.2	4.2	3.2	4.2
gfd/485 psig @ 36°C	7.0	6.2	5.7	5.75	4.5	4.4
gfd/600 psig @ 35°C	8.5	7.5	7.0	7.4	5.7	5.7

TABLE 63 (Continued)

Phase II

	10/22/70				10/29/70		11/5/70	
	Bank A		Bank B		Bank B	Bank A	Bank B	Bank A
	3 Mod	2 Mod	3 Mod.	2 Mod	5 Modules		5 Modules	
Solids, mg/l								
Raw feed					2366		2610	
Module feed	39,940		34,700		4638	20,448	5906	81,460
Permeate	2398	822	560	1412	332	1276	588	1845
Rej., percent	94.0	97.9	98.4	95.9	92.8	93.8	90.0	97.7
BOD, mg/l								
Raw feed					865		990	
Module feed	1610		1385		940	1568	1290	5290
Permeate	116	52	46	66	48	80	58	116
Rej., percent	92.8	96.8	96.7	95.2	94.9	94.9	95.5	97.8
COD, mg/l								
Raw feed					1410		1470	
Module feed	28,880		24,480		2810	14,660	2740	71,680
Permeate	278	109	89	147	60	125	69	181
Rej., percent	99.0	99.6	99.6	99.4	97.9	99.1	97.6	99.7
Sodium, mg/l								
Raw feed					542		594	
Module feed	7040		6160		1026	3580	1324	10,980
Permeate	852	292	202	515	121	500	195	672
Rej., percent	87.9	95.8	96.7	91.6	88.2	86.0	85.3	93.9
Color								
Raw feed					6000		7000	
Module feed	160,000		130,000		12,000	64,000	16,000	350,000
Permeate	225	35	25	60	10	45	10	100
Rej., percent	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
OD @ 281 nm								
Raw feed					17.06		19.78	
Module feed	380		330		33.8	66.0	44.2	902
Permeate	1.90	0.34	0.246	0.72	0.11	0.44	0.14	0.94
Rej., percent	99.5	99.9	99.9	99.8	99.7	99.3	99.7	99.9
pH								
Raw feed					8.32		9.22	
Module feed	7.12		6.80		7.28	7.40	7.20	7.38
Permeate	7.15	5.60	6.40	6.80	6.70	7.00	6.70	7.00
Resistance ohm-cm @ 25°C								
Raw feed					411		357	
Module feed	49		55		229	79	178	36.7
Permeate	252	678	961	397	1583	423	975	309
Temp., °C	33.5		33		34.5	34	31.5	33
Pressure, psig (in/out)	525/445		545/440		455/400	473/375	590/405	465/385
Permeate, ml/min	137	223	243	161	322	285	220	130
Velocity, ft/sec	3.2		4.2		4.2	3.2	4.2	4.2
gfd/600 psig @ 35°C	5.2		6.1		10.7	10.0	6.3	7.4

maintain the higher concentrations. This could only be realized by recirculation in this size installation. The two systems operated in parallel for the first week at inlet velocities of 4.2 feet per second in Bank A and at a lower velocity of 3.0 feet per second in Bank B. The feed concentration was maintained at 40 grams per liter in both banks.

After the first week, the modules in Bank B were operated on a feed liquor ranging from 5-10 grams per liter of solids, while Bank A was operated with feed concentrations in the range of 20-80 grams solids per liter (see Table 63). Product water flow and specific gravity of the feed were measured at least twice daily during this run. Solids concentrations and eventually also the osmotic pressure were determined experimentally and used to correct the flux rate data to a standardized level of 600 psig at 35°C. These corrections in flux rate data to a standard level were important in achieving close comparison with data for the following Phase III operations. Additionally, these corrections helped develop an understanding of the scatter in the data observed for Phase II and III where a wide range of osmotic pressure was occurring as the concentration increased from 1-10 percent solids. There were also problems apparent when attempting to interpret data in such a small system where recycling to achieve high levels of concentration resulted in low levels of draw-off of the concentrates in competition with some leakage of the pump seals.

It should be noted that the progression in concentration from low levels of concentration to high levels of concentration produced a characteristic increase in rejections at the higher levels of concentration during Phase I and II and progressing into Phase III. This observation has been made on numerous occasions over the past several years in these studies when concentrating these dilute pulp mill effluents. It can be concluded that low molecular weight materials, and especially volatile low molecular weight materials, are not well rejected in the first stage of processing at the lower levels of concentration. These materials are lost in the permeate from the first stage, and after they have passed from the system the levels of rejection are then observed to be markedly increased in later stages of concentration.

Phase III — Operations, Data and Results

Six new Havens modules of the latest design became available in October, 1970 in time for use and for comparison in the Phase III study. Five of these new modules were set up in series as a new Bank A to become a second stage in a 2-stage concentration system. The first stage was made up of ten of the older modules, all ten of which were hooked up in series in a single Bank B. (It should be noted that the designation of Banks A and B, as reported for Phase I, were reversed in the concentration runs for Phases II and III. Bank B then became the first stage and Bank A the second stage for the concentration runs.)

Detailed data for the Phase III operations are presented in Table 64. Concentrate from the first stage was about 0.7 percent to about 2 percent solids, and the second stage (A) achieved concentrations ranging to 8-16 percent solids. Rejections for all components were high, and for most determinations ranged upwards of 95 percent during these concentration studies in Phase III.

A rather uniform drop in flux rate was observed as the concentration increased from 1 percent solids to 11 percent solids. Data are tabulated to form a straight-line function as shown in Fig. 32. These flux rate data, when corrected to 35°C at 600 psig, were quite consistent over a 6-week period. The data summarized in Table 65 further develop the picture for the range of rejections which occur at various levels of solids concentration when processing caustic extraction bleach effluents from this kraft mill. These data result from careful continuing studies conducted with assay of a fairly large number of single and composite samples during this 3-month demonstration. The data are important in demonstrating that sustained high levels of performance can be expected in large installations. This conclusion has been difficult to prove out with most small laboratory operations on a single module or a few modules which are subject to interruptions and inconsistencies.

Figure 33 summarizes flux rate of the first stage with and without pulsing, and shows that rates on the order of 8.5 gfd can be maintained on a sustained basis for three weeks or more where the velocity approximates 2.8 feet per second. However, during the last three weeks we tried operating at lower velocity of 1.7 feet per second and found that the flux rates dropped to about 6-7 gfd. Pulsing this system periodically by reducing the pressure to near zero for 30 seconds or longer at periodic intervals of several hours or even at once per day levels restored the flux rate. The new modules in the second section (B) delivered a uniform flux rate with no need for pulsing during the six weeks they were in operation.

The problems of achieving high levels of recovery of the rejected solids, BOD_5, COD, sodium, and color in terms of optical density are summarized in Table 65. High levels of recycle are necessary in order to achieve high levels of concentration in small systems with only a few modules, such as was the case in these runs. The recoveries may appear lower than would be the case where a straight-through operation achieves much of the water removal at the lower level of concentration, and only relatively smaller amounts of water are removed as the concentration rises above 8 percent solids. The lower quality of the final effluents in a recycle operation reduces the numerical average for quality parameters to a greater extent than would be the case for analyses of samples from straight-through operation. Also, in the case of large-scale operations, the relatively small volumes of permeate in the final stages of concentration above 8 percent solids might be recycled to the feed if necessary to improve the degree of recovery of individual components in the concentrate and of turning out a clean, total permeate.

TABLE 64
PHASE III - DATA SUMMARY

	11/11/70		11/16/70		11/19/70		11/21/70	
	Bank B	Bank A	Bank B	Bank A	Bank B	Bank A	Bank B	Bank A
Solids, mg/l								
Raw feed	2726							
Module feed	7118	133,695	15,628	102,045	16,684	100,220	20,016	81,365
Permeate	255	627	782	2008	818	2090	806	2764
Rej., percent	91.2	99.8	95.0	98.0	95.1	97.9	96.0	96.6
BOD, mg/l								
Raw feed	175							
Module feed	310	5200	795	5300	2120	5480	1620	4740
Permeate	44	163	37	127	71	141	78	180
Rej., percent	85.8	96.9	95.3	97.6	96.6	97.4	95.2	96.2
COD, mg/l								
Raw feed	1600							
Module feed	4360	117,000	10,260	80,750	12,500	78,265	16,100	67,000
Permeate	95	375	97	285	107	255	111	295
Rej., percent	97.8	99.7	99.0	99.6	99.1	99.7	99.3	99.6
Sodium, mg/l								
Raw feed	604							
Module feed	1632	18,280	2728	15,680	2760	15,040	3100	11,080
Permeate	211	838	495	654	276	710	280	740
Rej., percent	87.1	95.4	81.8	95.8	90.0	95.3	91.0	93.3
Color								
Raw feed	7000							
Module feed	20,000	650,000	40,000	400,000	50,000	400,000	90,000	350,000
Permeate	10	200	20	150	20	125	25	125
Rej., percent	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
OD at 281 nm								
Raw feed	19.4							
Module feed	48.8	1448	138.4	1100	152	1036	206.4	896
Permeate	0.17	2.16	0.232	1.62	0.245	1.316	0.288	1.45
Rej., percent	99.6	99.8	99.8	99.8	99.8	99.9	99.9	99.8
pH								
Raw feed	10.4							
Module feed	7.32	7.30	7.22	7.39	6.83	7.20	7.45	7.41
Permeate	6.51	7.08	6.61	6.92	6.55	6.82	6.71	7.04
Resistance ohm-cm at 25°C								
Raw feed	354							
Module feed	163	28	96	29	103	29	94.6	35.2
Permeate	892	252	771	307	721	317	686	274
Temp., °C	30	34.5	30.5	35	31	34.5	31	34.5
Pressure, psig (in/out)	500/375	770/565	520/390	730/535	495/390	740/540	495/395	710/530
Permeate, ml/min	183	229	206	233	228	208	156	254
Velocity, ft/sec	3.2	4.2	3.2	4.2	3.2	4.2	3.2	4.2
gfd/600 psig at 35°C	6.4	4.0	7.1	4.7	7.8	4.0	5.4	5.3

TABLE 64 (Continued)
PHASE III - DATA SUMMARY

	11/23/70		12/1/70		12/2/70		12/7/70	
	Bank B	Bank A	Bank B	Bank A	Bank B	Bank A	Bank B	Bank A
Solids, mg/l								
Raw feed	2646		2454		2636		3242	
Module feed	22,018	118,480	19,930	100,560	9288	132,630	7384	159,432
Permeate	685	2038	690	1789	693	2833	647	3026
Rej., percent	96.9	98.3	96.5	98.2	92.5	97.9	91.2	98.1
BOD, mg/l								
Raw feed	215		220		185		253	
Module feed	1272	8350	925	4600	512	6250	447	8150
Permeate	62	144	40	138	48	235	61	210
Rej., percent	95.1	98.3	95.7	97.0	90.6	96.2	86.4	97.4
COD, mg/l								
Raw feed	1584		1266		1228		---	
Module feed	17,380	100,000	15,920	77,500	5620	104,500	5560	137,500
Permeate	104	335	120	315	95	446	113	449
Rej., percent	99.4	99.7	99.2	99.6	98.3	99.6	98.0	99.7
Sodium mg/l								
Raw feed	608		604		690		662	
Module feed	3530	16,000	3224	13,440	1948	19,040	1380	20,120
Permeate	250	710	246	594	248	974	234	1002
Rej., percent	92.9	95.6	92.4	95.6	87.3	94.9	83.0	95.0
Color								
Raw feed	7500		4000		5000		8000	
Module feed	100,000	500,000	72,000	320,000	24,000	400,000	22,000	640,000
Permeate	25	150	20	125	15	175	20	275
Rej., percent	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
OD @ 281 nm								
Raw feed	20.4		15.56		14.40		26.44	
Module feed	232	1332	196	1100.8	63.6	1395	59.6	1872
Permeate	0.28	1.71	0.284	1.49	0.201	2.31	0.21	2.80
Rej., percent	99.9	99.9	99.8	99.9	99.7	99.8	99.6	99.8
pH								
Raw feed	10.04		10.62		10.02		9.52	
Module feed	7.40	7.28	6.90	7.05	6.75	6.58	7.30	7.18
Permeate	6.70	6.98	6.20	6.30	6.20	6.42	6.70	7.10
Resistance ohm-cm @ 25°C								
Raw feed	358		358		278		359	
Module feed	86.9	28.2	94	31	130	24	166	25.7
Permeate	790	298	810	350	805	258	816	219
Temp., °C	29	32.5	30	35	31	35	29	32
Pressure, psig (in/out)	525/480	780/575	490/405	685/455	475/395	810/580	480/450	795/650
Permeate, ml/min	248	224	224	168	274	205	277	170
Velocity, ft/sec	2.6	4.2	3.2	4.2	3.2	4.2	2.2	3.2
gfd/600 psig at 35°C	7.7	4.1	8.5	[1]4.6	9.5	[1]3.2	6.1	[2]2.3

TABLE 64 (Continued)
PHASE III - DATA SUMMARY

	12/9/70		12/14/70		12/15/70		12/15/70	
	Side B	Side A	Side B	Side A	Side B	Side A	Side B	Side A
Solids mg/1								
Raw feed	2648							
Module feed	8688	116,602		93,156		62,548	5010	30,436
Permeate	619	2014		3084		1975	442	7328
Rej., percent	92.9	98.3		96.7		96.8	91.2	75.9
BOD, mg/1								
Raw feed	183							
Module feed	542	5825		5350		3600	312	1612
Permeate	58	132		145		111	48	82
Rej., percent	89.3	97.7		97.3		96.9	84.6	94.9
COD, mg/1								
Raw feed	1432							
Module feed	5635	91,600		41,600		42,400	2045	22,200
Permeate	91	259		266		206	77	145
Rej., percent	98.4	97.7		99.4		99.5	96.4	99.4
Sodium mg/1								
Raw feed	640							
Module feed	1708	13,160		11,840		8920	1155	5530
Permeate	222	670		830		556	148	458
Rej., percent	87.0	94.9		93		93.8	87.2	91.4
Color								
Raw feed	6000							
Module feed	26,000	440,000		240,000		160,000	6665	144,000
Permeate	10	100		70		53	25	65
Rej., percent	99.9	99.9		99.9		99.9	99.6	99.9
OD at 281 nm								
Raw feed	17.96							
Module feed	68.4	1208		1120		656.8	33.95	298.4
Permeate	0.199	1.30		1.61		1.00	0.195	0.560
Rej., percent	99.7	99.9		99.9		99.8	99.6	99.9
pH								
Raw feed	16.51							
Module feed	7.35	7.42		7.21		7.26	7.10	7.30
Permeate	6.81	7.10		7.02		6.95	6.36	7.10
Resistance ohm-cm at 25°C								
Raw feed	337							
Module feed	149	32.6		37.2		44.6	205	69.5
Permeate	852	310		267		439	1218	427
Temp., °C	28	30		33		33	31	33
Pressure, psig (in/out)	510/490	705/555		740/620		755/630	515/490	710/590
Permeate, ml/min	273	204		312		312	196	340
Velocity, ft/sec	2.2	3.2		3.2		3.2	2.2	3.2
gfd/600 psig at 35°C	8.5	4.5		5.9		5.75	5.8	7.0

Phase III Data from 2-Stage Concentration

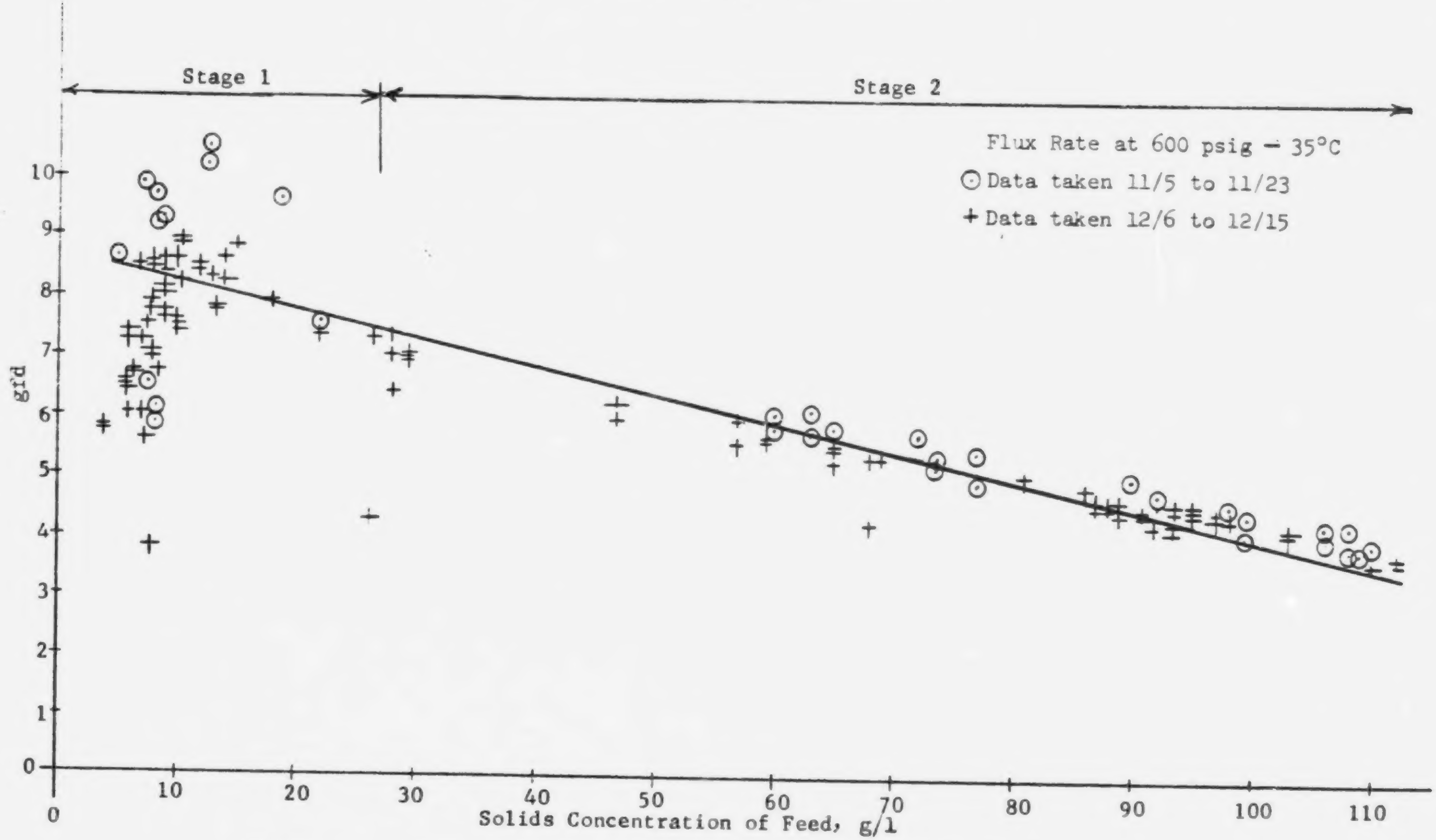


Figure 32. Decrease in Flux Rate with Increase in Solids Concentration

TABLE 65

RANGE OF RECOVERY OF REJECTED COMPONENTS AT VARIOUS LEVELS OF CONCENTRATION
(Percent)

Solids, g/l	3.0-9.3	15.6-22.0	81.4-118.5	132.6-159.4
Number of determinations	4	5	7	3
Solids	91.2-92.5	95-96.9	96.6-98.3	97.9-99.8
BOD_5	85.8-90.6	95.1-95.7	96.2-97.7	96.2-97.4
COD	97.8-98.4	99.0-99.4	99.6-99.7	99.6-99.7
Sodium	83.0-87.3	81.8-92.9	93.3-95.8	94.9-95.4
Color	99.9	99.9	99.9	99.9
Optical density at 280 nm	99.6-99.7	99.8-99.9	99.8-99.9	99.8-99.9

The overall recoveries of rejected material experienced in this 3-month field trial, and as reported in Table 65, are especially interesting in view of counter observations of relatively poor rejections, which may often be observed in early stages of concentrating wastes containing low molecular weight or small molecular size material which can pass the membrane. Similar loss in rejections may also appear at high levels of recycle in the upper limits of concentrating some wastes (often observed when the concentration reaches 15 percent solids or equivalent levels, with resultant high osmotic pressure). Low molecular weight material, and particularly volatile low molecular weight material, may pass through the membrane rather freely in early stages of concentration and may substantially reduce rejection of the system, as is the case of the BOD_5 rejections dropping below 70 percent if acetic acid, methanol, H_2S, and similar components are present. However, for most wastes studied this is a transitory loss in rejections which may have small effect on a total concentration system. Elsewhere it was noted that reverse osmosis of evaporator condensates, with high levels of volatiles, is a notable exception, and in that case it is necessary to neutralize acetic acid to achieve good rejections of the acetate salts and good BOD reduction.

Loss in rejections when the osmotic pressure reaches high levels is apparently a limiting factor on membrane performance and needs careful study and definition for each type of waste. In this study on the caustic extraction bleach effluent, the limiting level may be in the neighborhood of 15 percent solids, but the volume of permeate containing

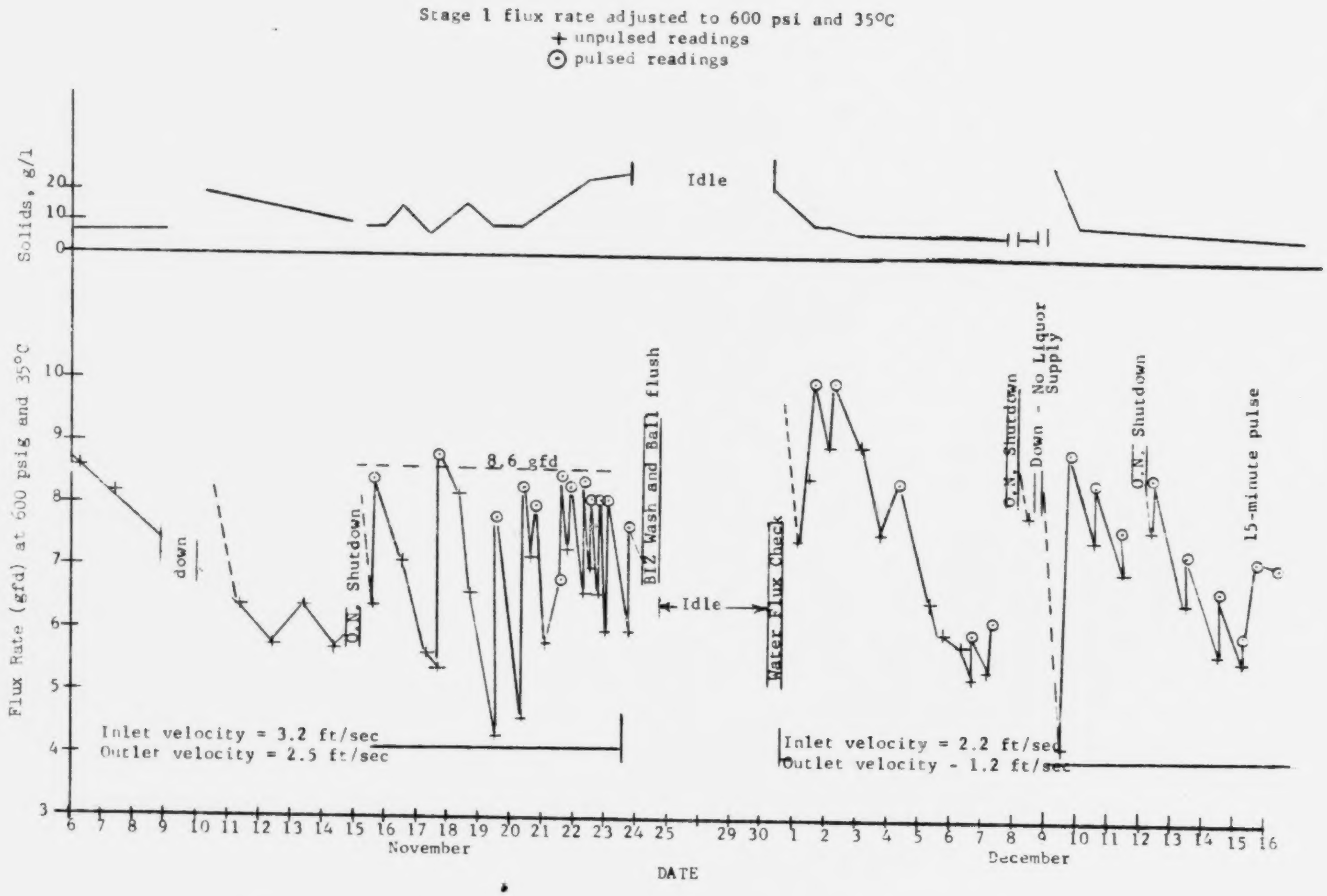


Figure 33. Comparison of Flux Rates with and Without Pulsing

poorly rejected solids may be sufficiently low even at that level of concentration so as to permit recycle of the permeate to earlier stages of feeding the system where rejections are high. These studies have not yet been carried far enough to thoroughly test this concept for achieving the higher levels of concentration above about 12 percent solids.

One of the criteria in achieving efficient operation of the equipment and for interpreting the results of analytical studies has been based in these studies on development of an osmotic pressure to solids relationship upon which observed flux rates could be corrected to a standard level for comparative evaluation. Such a relationship is shown in Fig. 34, in which the applied correction used in these studies is indicated as one of the four curves on this graph.

Development of operating parameters for reverse osmosis concentration for this caustic extraction bleach effluent from kraft pulping required a quick method of developing the solids concentration as based on determination of specific gravity at 20°C. Availability of this curve (Fig. 35) helped substantially in operating the equipment efficiently and consistently during the final stages of the 3-month run at Cloquet.

Consistent and reliable performance of the equipment was achieved in this run as the operating know-how developed. The demonstration has shown that alkaline extraction KBE can be concentrated from 30 to 50 times or more by reverse osmosis on the basis of continuous operation and without the drastic variations and declines in flux rate experienced on smaller-scale studies conducted in the early phases of this overall project in the laboratory and in shorter term pilot studies. The overall operations on site at Cloquet and the various laboratory studies conducted concurrently in Appleton clearly show that this bleach plant effluent can be successfully concentrated at high levels of treatment efficiency and with sustained operating efficiency in a continuous operation of membrane equipment.

SUPPLEMENTARY STUDIES

More than five years of preliminary laboratory and small pilot-scale studies of membrane processing of various pulp and paper mill effluents preceded this demonstration run and provided the base upon which a successful demonstration could be planned and executed. It is not the purpose of this report to present a detailed review, but certain areas of those studies provide back-up experience in the field of processing kraft pulping and bleaching effluents.

Processing Mixed First Stage Chlorine and Second-Stage Alkaline Extraction Effluents

Reverse osmosis concentration processing of mixed first and second-stage bleach effluents presents obvious advantage in terms of reduced pretreatment costs for pH adjustment and perhaps also temperature

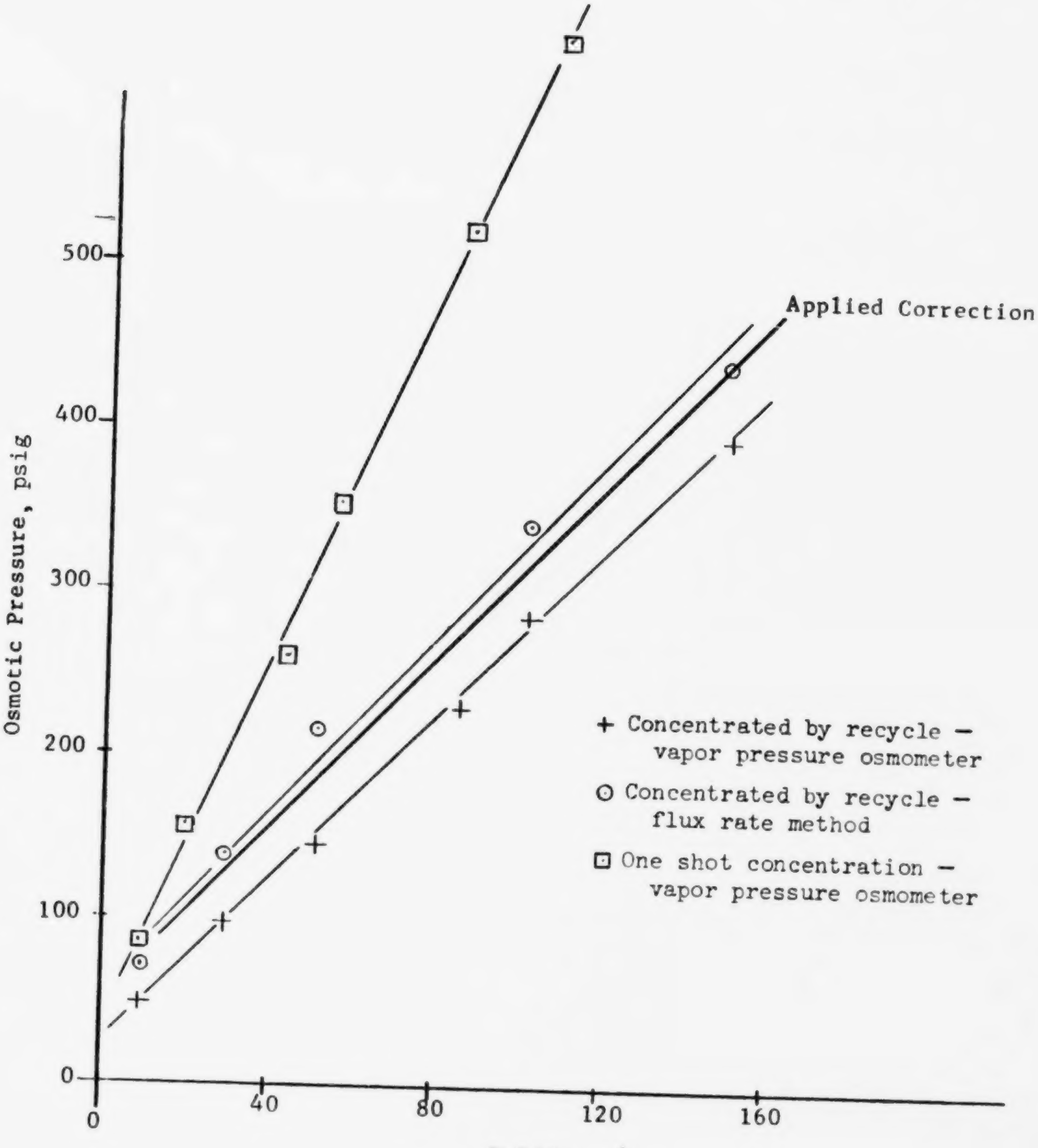


Figure 34. Osmotic Pressure of Caustic Extraction Effluent

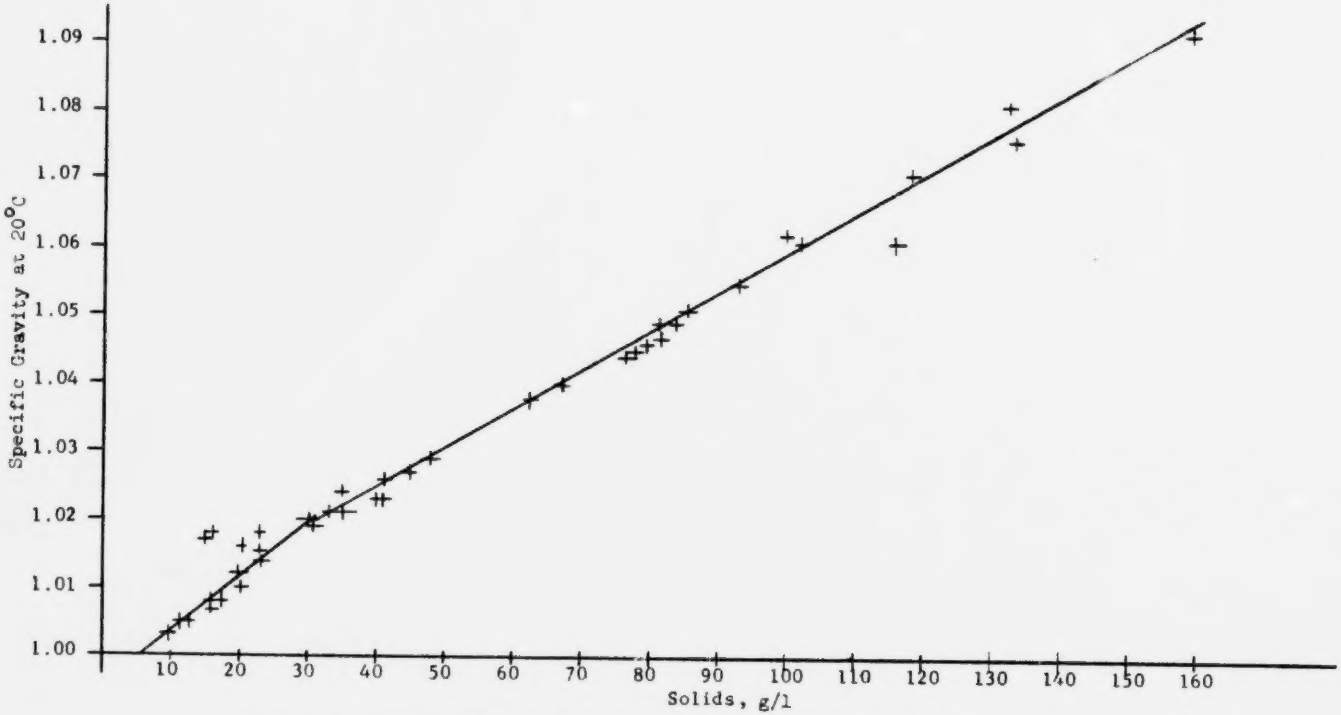


Figure 35. Total Solids as Function of Specific Gravity of Alkaline Extraction KBE

balancing. The cellulose acetate membranes available for reverse osmosis at the time of conducting these studies required adjustment of pH within the range of 3.0 to 7.0, and a temperature range of 35-40°C has normally been recommended for attaining maximum flux rates and to avoid heat-accelerated membrane degradation by hydrolysis and related reactions.

Unfortunately, the first-stage chlorine KBE available at the Cloquet mill was highly dilute as shown by the following typical analysis:

Solids	1.303 g/l
BOD_5	102 mg/l
Chlorine	472 mg/l
Color (Co or Pt)	100
OD at 280 nm	2.1
pH	2.15-2.4
Temperature	17-19°C

There seemed to be no practical way in which to secure needed quantities of 500 to 1500 gallons daily of a more concentrated first-stage chlorine KBE without substantial process modification and serious disruption of mill operations.

The dilute chlorine stage liquor at one-half the solids concentration of the second-stage caustic extraction effluent could not be used as feed in our demonstration without serious cut-backs in the production of higher concentrations of final product. Attempts to set up the main demonstration on combined effluents had to be set aside in favor of work only on the caustic extraction liquor.

However, a small-scale short-term test run was made using a single 2-tube module especially fabricated for tests on small volumes of a few gallons. Chlorine stage KBE and also caustic extraction stage KBE, which had been obtained by manually pressing high density pulp from the towers, were mixed and processed in this special reverse osmosis concentration run. The caustic extraction feed sample had a solids concentration of 4.57 grams per liter, and the chlorine bleach effluent was still very dilute at 1.24 grams per liter. These were mixed in the proportion of 3 parts of the first-stage chlorine effluent and one part second-stage caustic extraction product to approximate the volumes being sewered at this mill. The mixture had a pH of 2.0 and a solids concentration of 2.1 grams per liter. Table 66 summarizes the data obtained on this small-scale test run which was carried to the point of concentrating more than 10 times to achieve about 2.5 percent solids (24.64 grams per liter). At that level the osmotic pressure, due to content of NaCl, was found to be sufficiently high to have reduced the effective driving force and to have caused a substantial reduction in flux rate of more than 50 percent from 14.8 gfd to 6.4 gfd at 600 psig. Other experience would indicate the drop in flux rate might be taken care of with higher operating pressures and higher velocities as the concentration increases, but this preliminary run could not be extended to evaluate that point. The

TABLE 66

REVERSE OSMOSIS PROCESSING OF COMBINED FIRST
AND SECOND-STAGE BLEACH PLANT EFFLUENTS

	Dissolved Solids		BOD_5		Optical Density		Sodium			Flux Rate @ 600 psig and 40°C
	g/1	Rej., percent	mg/1	Rej., percent	@ 280 nm	Rej., percent	mg/1	Rej., percent	pH	
Chlorination effluent	1.24		190		4.28		77.5		1.75	
Caustic extract effluent	4.57		279		32.2		1188		10.98	
Combined effluents	2.117	85.6	219	21	10.69	96.4	339	71.7	2.03	14.8
	5.393	91.5			24.4	97.9			2.20	11.5
	9.96	98.5			50.0	98.8			2.65	9.5
	17.84	89.7			99.5	99.4			3.22	7.5
Final concentrate	24.64	88.8	922	78.4	144	99.5	1540	31.6	3.22	6.4

advantages apparent in processing combined effluents remain as important objectives for further study.

STUDIES ON KRAFT PULP WASH WATERS

Extensive laboratory and pilot and also field test runs were made on concentration of the wash water from the countercurrent washer and from the rewasher in the kraft pulping operations ahead of the bleach plant at this mill. At the time these tests were initiated, this was considered to be one of the most serious pollution problems prevailing at the Cloquet mill, but later on in the course of these studies the mill management decided to make process changes which would eventually recycle and eliminate this type of pulping spent liquor. The preliminary RO studies were terminated. A brief accounting of the rewash water concentration trials is reviewed in the following paragraphs, since the experience was in many ways valuable. The rewash water was an especially difficult substrate for processing by reverse osmosis in terms of apparent fouling and a resultant decrease in flux rates through the membrane. These results were, however, not consistent in all runs. Some samples sent to Appleton were relatively easy to process, and then other shipments would give serious levels of fouling and flux reduction. The critical importance of maintaining optimum velocities was not apparent at that time, and overall average velocities may have been critically low with so many modules operating in series.

Preliminary studies using two different types of cellulose acetate membranes showed excellent levels of rejection for all components studied, as shown in Table 67.

TABLE 67

REJECTION DATA FOR REVERSE OSMOSIS OF KRAFT PULP WASH WATER
[Moderately Tight (3) and Tight (5) Membranes]

	Type 3, percent	Type 5, percent
Solids	95	99
Sodium	96	99
OD at 280 nm	97	98
BOD_5	90	95
COD	95	98

The moderately tight cellulose acetate membrane (Type 3), normally used in most of these studies, was compared with the tighter type No. 5 membrane from this manufacturer. The average BOD removal was above

90 percent for both membranes. Tables 68 and 69 provide more detailed operating data for a preliminary field run conducted at Cloquet during the summer months of 1968 for processing these wash waters.

TABLE 68

COMPARATIVE FLUX RATES VS. SOLIDS CONCENTRATIONS OF KRAFT WASH WATER

Operation of Preliminary RO Unit at
Northwest Paper Company, Cloquet, Minnesota

Period No.	Operating Time Totalized, hours	Concentration Feed, solids g/l	Flux Rate, gfd adjusted to 35°C Type 3 Used Modules	 Type 3 New Modules	 Type 5
		Feed from Countercurrent Washer			
1	101	9.0	7.7	--	4.7
2	161	14.8	4.8	--	3.2
3	162	19.8	4.9	12.6	3.2
4	219	13.6	5.0	12.2	2.4
		Feed from Rewasher			
5	61	1.05	--	20.1-8.0	--
6	232	0.95	--	9.8-3.5	--
7	325	0.9	--	12.4-3.3	--
		Recycle Operation			
8	484	1.67	--	4.3-2.4	--
9	576	2.61	--	5.2-3.1	--
10	596	6.39	--	4.5-2.6 untreated module	

The equipment and the size of the operations were similar to the later runs conducted on the alkaline extraction bleach effluent. These runs totaled 815 hours, with a number of interruptions when it was decided to return to the laboratory to study individual problems between runs at Cloquet. Table 68 compares the flux rates observed at various levels of solids concentration and with Types 3 and 5 membranes in previously used and in new modules. The first section provides data for the liquor feed from the countercurrent washer, which was diluted with river water to approximately 1 percent solids, while the second section provides data from processing rewash water, both straight-through with the concentrate recycled. Although wide variations in flux rate were evidenced.

TABLE 69

ANALYTICAL DATA PILCT UNIT RUN ON
KRAFT PULP WASH WATER

	Operating Time, hours	Solids, g/l	Sodium, mg/l	BOD_5, mg/l	COD, mg/l	Optical Density at 281 nm	pH	Specific Resistance, ohm-cm
1. Feed	101	9.03	1720	2585	8,310	70	7.67	233
Permeate 3		0.71	212	365	493	2.40	7.73	1,140
Permeate 5		0.43	9	165	146	0.93	6.62	11,600
Concentrate		14.47	2500	3910	12,800	104	8.58	--
Rej. Type 3, percent		92.1	87.7	85.9	94.1	96.6	--	79.6
Rej. Type 5, percent		95.2	99.2	93.6	98.2	98.7	--	98.0
2. Feed	161	14.81	2940	3305	14,290	115	7.23	283
Permeate 3		0.32	79	224	391	3.10	6.38	2,830
Permeate 5		0.16	29	174	286	2.58	6.40	6,600
Concentrate		19.64	3630	4580	18,600	150	7.35	240
Rej. Type 3, percent		97.8	97.3	93.2	97.3	97.3	--	90
Rej. Type 5, percent		98.9	99.0	94.7	98.0	97.8	--	97.7
3. Feed	162	19.84	3380	5340	18,631	160	7.33	113
Permeate 3		1.73	430	728	1,199	5.26	7.05	600
Permeate 5		0.74	201	473	689	4.19	6.58	1,330
Concentrate		25.80	4480	6490	23,850	208	7.38	1,103
Rej. Type 3, percent		91.3	87.3	86.4	93.6	96.7	--	81.2
Rej. Type 5, percent		96.3	94.1	91.1	96.3	97.4	--	91.5
4. Feed	219	13.58	2190	2340	10,620	82.5	7.80	310
Permeate 3		0.92	342	464	815	4.14	7.35	1,200
Permeate 5		0.15	20	169	234	2.00	7.90	11,000
Concentrate		17.62	3250	3515	16,400	125	7.42	228
Rej. Type 3, percent		93.2	84.4	80.2	92.3	95.0	--	74.2
Rej. Type 5, percent		98.9	99.1	92.8	97.8	97.6	--	97.2
5. Feed	263	1.05	202	160	836	6.28	--	1,460
Permeate 3		0.05	11	25	53	0.27	6.28	21,000
Concentrate		1.73	348	254	1,405	10.60	7.60	960
Rej. Type 3, percent		95.3	94.6	84.4	93.7	95.7	--	93.0
6. Feed	232	0.957	514	129	796	6.50	7.35	2,420
Permeate 3		0.045	14	27	46	0.24	7.20	18,000
Concentrate		1.039	540	126	840	7.10	7.55	2,160
Rej. Type 3, percent		95.3	97.3	79.1	94.2	96.3	--	86.6
7. Feed	375	0.90	197	192	760	5.8	6.49	2,650
Permeate 3		0.038	9.8	26	45	0.20	6.10	32,000
Concentrate		1.00	217	218	826	6.2	6.99	2,450
Rej. Type 3, percent		95.8	95.0	86.5	94.1	96.5	--	91.7
8. Feed	484	1.67	400	306	1,490	11.1	7.05	1,285
Permeate 3		0.059	16	32	28	0.36	6.50	16,200
Concentrate		1.88	470	348	1,730	12.3	7.02	1,160
Rej. Type 3, percent		96.5	96.0	89.6	98.1	96.8	--	93.1
9. Feed	576	2.61	490	212	396	10.0	7.25	865
Permeate 3,		0.067	15	15	39	0.26	7.79	14,500
Concentrate		2.78	490	216	1,278	10.0	7.25	645
Rej. Type 3, percent		97.4	96.9	92.9	90.2	97.4	--	94.0
10. Feed		6.39	1660	645	2,493	20.0	8.10	485
Permeate 3		0.152	41	35	86	0.48	7.25	7,450
Concentrate		6.94	1990	645	2,665	21.0	7.30	292
Rej. Type 3, percent		97.6	97.5	94.8	96.6	97.6	---	93.5

Perm A is from preconditioned modules. les.
Perm B is from untreated modules.

Figure 36 shows the substantial reduction in flux rates experienced with the kraft rewash waters over the 580 hours that this dilute wash water was processed. This loss in flux rate was not affected by velocities up to 2.5 ft/sec or pressure pulsing for 1 minute every hour. Higher velocities have since been found effective in reducing such fouling but the work was terminated short of a full trial on rewash water.

Table 69 provides rejection data for these studies on the countercurrent wash water and on the rewash water. All rejections were excellent throughout these runs, although no attempt was made to carry the concentrations to high levels of concentration in these preliminary runs. Part of the concentrate was recycled while processing rewash water to increase concentration from 0.1 percent solids to a more representative 0.5 percent solids. In between the field runs at Cloquet during these pulping rewash water studies, a number of laboratory trials were made in an attempt to develop methods of pretreatment which would improve the flux rate performance. Various additives and pretreatment methods were tested; some were found to be moderately successful in reducing the fouling but no means of maintaining steady state flux rate had been found at the time it was decided that rewash waters would be eliminated.

DISCUSSION

This demonstration provided the first available operating data from sustained runs on membrane processing of bleach plant effluents. The emphasis and most of the data desired from the studies on the second-stage alkaline extraction KBE are usually considered to be of most concern in maintaining effluent quality standards. However, the processing of combined effluents can in all probability be developed as a feasible concentration process with membrane systems if the starting feed volume can be reduced to practical levels below 10,000 gal./ton pulp.

High levels of salt (NaCl) concentration may appreciably raise the osmotic pressure, and therefore need may arise for maintaining higher operating pressures in the system to override that higher osmotic pressure. But extensive experience is available from worldwide salt water conversion studies to lend confidence to the conclusion that higher levels of salt can be successfully handled.

The field demonstration helped to prove out the methods developed in some three years of preliminary studies for maintaining sustained and practical levels of flux through the membrane based on:

> Maintaining velocities and turbulence at levels sufficiently high to avoid concentration polarization and fouling of the membrane.

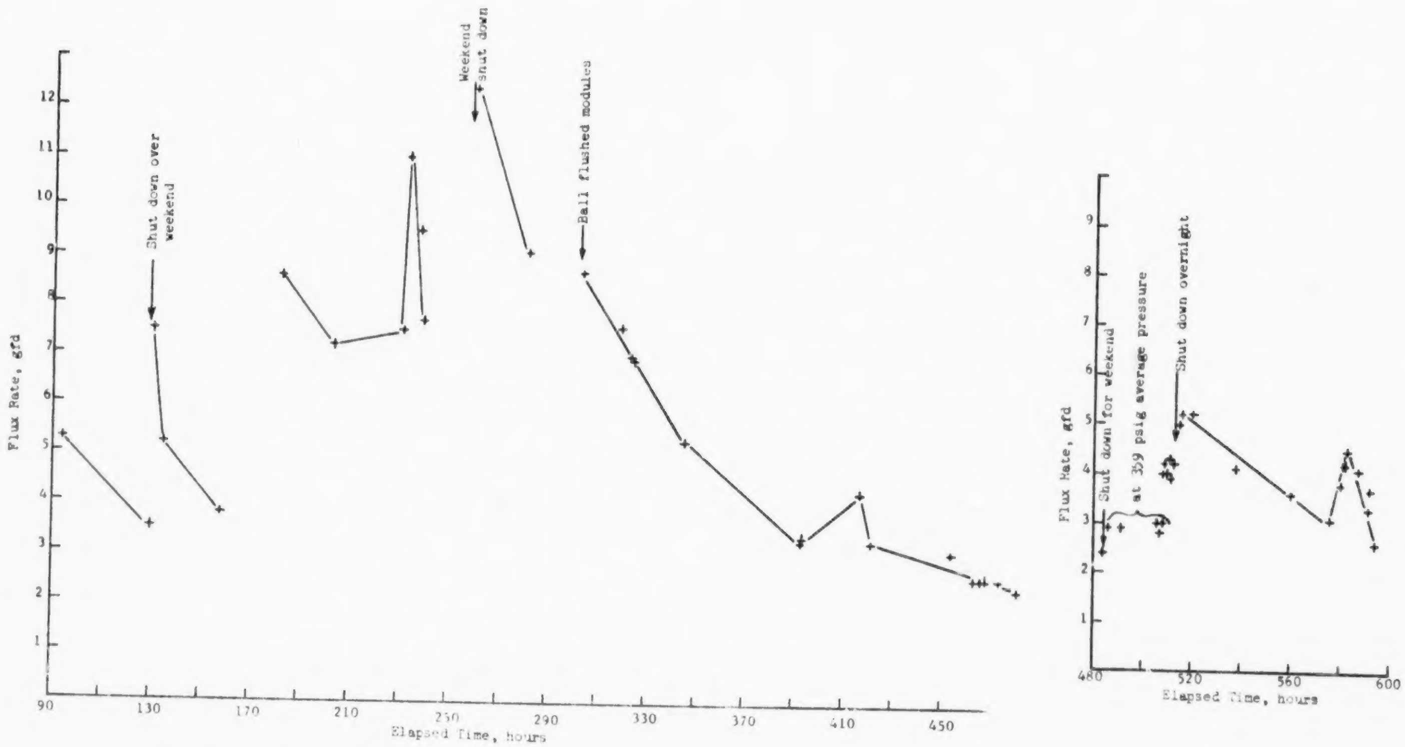


Figure 36. Flux Rate History While Processing Kraft Rewash Water with the Pilot Unit

Pulsing (periodic pressure reduction) to clear fouling and membrane compaction.

No elaborate systems or procedures for pretreating the bleach effluent were required beyond nominal adjustment of pH and temperature and screening (50 mesh) to remove gross amounts of fiber and particulate matter.

The introduction to this report cited the importance of trends toward substantial reduction in the volumes of water used in the total process of bleaching and washing of bleached pulps. Present stage development of reverse osmosis equipment still involves relatively high capital and operating charges. Pulp mills and bleach plants normally expect the cost of fresh process water to be in the range of 3 to 10 cents per thousand gallons. Reverse osmosis has been aimed toward costs of less than 50 cents per thousand gallons of water removed, and some manufacturers look forward to costs as low as 25 cents per thousand gallons eventually, but present-day evaluations to be discussed in more detail in Section X still show costs to be more realistically in the range of 50 cents to $1.50 per thousand gallons at this early stage of commercial development. Water recovered by reverse osmosis therefore costs several times as much as fresh incoming treated process water. Obviously, the cost of treating outgoing waters for pollution control must bear most of the cost for complete treatment of the bleach plant effluents. Most kraft bleaching operations have a BOD_5 output in the range of 30 to 50 pounds per ton of product and substantial color and salinity problems. Secondary treatment designed to reduce the BOD_5 by the biooxidation route would cost about 4 to 5¢ per pound BOD_5 or in excess of $1.00 per ton pulp (or in a 5000 gallon per ton flow, about 20 cents per thousand gallons). Color removal has been an especially difficult problem, with charges indicated to be on the order of $2.90 per ton, or nearly 60 cents per thousand gallons at flows of 5000 gallons per ton[22]. Of more importance eventually may be the recovery of 200 to 300 pounds of NaCl from each ton of chlorine bleached pulp. A substantial credit for reverse osmosis concentration processing may be possible by recovery of bleaching chemicals in addition to pollution control and water reuse credits.

The economies of applying reverse osmosis to processing of pulp and paper mill effluents are discussed more fully in Section X.

CONCLUSIONS

Substantial field trials of reverse osmosis concentration processing of second-stage caustic extraction bleach effluents have been successfully conducted at flow rates on the order of 1500 gallons daily for a 3-month period.

Flux rates of 7 to 8 gfd can apparently be maintained indefinitely in concentrating this bleach effluent in the range of 0.2 to 10 percent solids concentration.

No elaborate or extensive pretreatment of the bleach effluent beyond nominal amounts of temperature adjustment, pH control, and suspended solids removal (50-mesh screen) seem to be required.

Treatment of combined bleach effluents seems also to be a feasible operation on the basis of smaller-scale trials, although higher levels of NaCl content may raise the osmotic pressure of the concentrates, and hence require somewhat higher (but still feasible) operating pressures to perhaps 800 psig.

The future economics of more complete bleach effluent processing may be competitive and favorable in terms of:

- Recovery of reusable water.
- More complete pollution control treatment to remove color, foam, inorganics, and resistant organics, as well as BOD_5.
- Recovery of NaCl from bleach effluents.
- Possibilities for ultimate regeneration of Na and Cl bleach chemicals.

FIELD DEMONSTRATION NO. 5

CONCENTRATION OF CHEMIMECHANICAL PULP WASH WATERS BY REVERSE OSMOSIS

This subsection describes laboratory and field studies conducted as Demonstration No. 5 under Federal Research and Demonstration Grant 12040 EEL. The demonstration field trial was conducted at the Locks Mill of Appleton Papers, Inc., a subsidiary of the National Cash Register Company, in Combined Locks, Wisconsin. The recently modernized pulp mill is representative of one of the newer developments in high-yield pulping employing a chemical pulping process in a combination with mechanical pulping. The method of pulping is usually referred to as the chemimechanical (CM) process. More than 90 percent of the original wood raw material is recovered as usable fiber for high-grade specialty papers, and especially for telephone directory papers. High-yield pulping processes utilize much more of the wood raw material than can normally be expected for conventional chemical pulping systems, and with resultant substantial reductions in water, air, and solids waste disposal problems.

However, the portion of the wood which is fully dissolved or partially solubilized in this high-yield pulping process presents a substantial disposal problem in the mill program of compliance with effluent quality standards. This new CM process is still in early stages of commercial development and pulp production methods remain to be standardized. Procedures will have to be developed for solving the pollution problems. This demonstration has been directed to evaluation of one possible route for recovery and concentration of the dilute wash from secondary refining and washing of the pulp. Such a concentrate could then be processed for disposal together with the strong spent liquor from the

1st stage of pressafining of the pulp. The various stages of refining and washing of the pulp on conventional belt filters and related washing equipment results in substantial dilution of the wash water effluents.

The first objective in undertaking this field demonstration was to survey the various steps of refining and washing the pulp in this recently revised pulp mill. It was desired to establish the most effective point for collecting most of the solubilized or partially solubilized material being washed from the pulp in the least possible volume which could be economically collected and fed to a concentrating system based on RO.

The total volume of the very dilute wash waters presently being discharged ranges upwards of 1,250,000 gallons per day, with a total solids content of less than 0.2 percent. Preliminary sampling indicated the principal flow of pulp wash waters, if isolated from other more dilute flows, might have a volume of about 550,000 gallons. Analysis of small samples of such wash waters is summarized in Table 70, and calculations of the apparent pollution load are provided in the second and third columns.

Further isolation and recovery of the strongest wash waters in a commercial operation might be expected to further reduce the volume and still collect as much as 80 percent of the solubles and semisolubles. The resulting volume of several hundred thousand gallons of strong spent liquor might then be expected to be especially suitable for RO concentration, starting with a feed at about 1 percent solids and increasing the concentration to about 10 percent solids. That intermediate concentrate at 10 percent solids from the membrane process could then be evaporated economically by conventional methods, along with the strong, digester liquors to yield a final concentrate containing substantially all of the pollution load from the pulp mill. Recycle of the reclaimed permeate water recovered by the RO system back into the final stages of pulp washing could be expected to further improve the recovery of the solubilized and partially solubilized materials to the point of achieving nearly 100 percent closure of the pulp mill cooking and washing system.

This demonstration, No. 5, was then designed with those objectives in mind. The following pages of reporting cover the various stages of developing the individual unit operations in the attempt to achieve a practical system of RO concentration for the dilute pulping wash waters from this pulp mill.

The Chemimechanical Pulping Process

This high-yield pulping process is characterized by mild soaking in a continuous chemical cook to soften the chips, followed by mechanical refining to separate the fibers of lignocellulosic materials. Figure 37 provides a flow sheet of the CM pulping system for the Locks Mill, with inclusion of an RO pilot treatment system. This mill, at the time of making these field trials, was rated at 200 tons pulp per day (85 tons unbleached and 115 tons bleached). The mill pulps aspen "hard" wood (often referred to as poplar), by an alkaline sodium sulfite continuous quick cook of the chips in a high consistency pulping operation with primary and secondary refining, followed by a low consistency cleaning and washing operation. The principal effluent streams from the mill include the pressafiner liquor flow and a combined effluent wash water from the final stages of washing and refining of the pulp.

TABLE 70

POLLUTION LOADING OF DILUTE PULP WASH WATER FROM A CHEMIMECHANICAL PULP MILL

Discharge volume = 550,000 gallons per day[a]
Discharged per ton of pulp = 2750 gallons
Production = 200 tons per day

	Concentration		
Constituent	Milligrams per Liter	Pounds per 1000 Gallons	Pounds per Day
Solids	6120	51.0	28,000
BOD_5	1980	16.5	9,070
COD	7050	58.7	32,300
Volatile acid	1369	11.4	6,270
Sodium	832	6.9	3,800

Temperature = 65-70°C
pH = 7.5-8.2

---

[a] The preliminary estimate of the volume of dilute pulp wash water does not include the flow of digester strength spent liquor.

The pressafiner liquor samples contained about 7 percent of total solids in terms of both the organic and inorganic materials. One route to disposal might be based upon a system to concentrate and burn the comparatively small flow (43,000 gallons per day) of pressafiner liquor containing about 25,000 pounds of total solids, 11,000 pounds of BOD_5, and 5100 pounds of sodium. Preliminary tests indicated RO flux rates for the further concentration of the pressafiner liquor from the 7 percent solids level might be very low, and would not be economically feasible under the conditions studied. Later in the study the pressafiner liquors were found to have high osmotic pressure due to content of Na_2SO_4. Further studies at higher velocities and higher operating

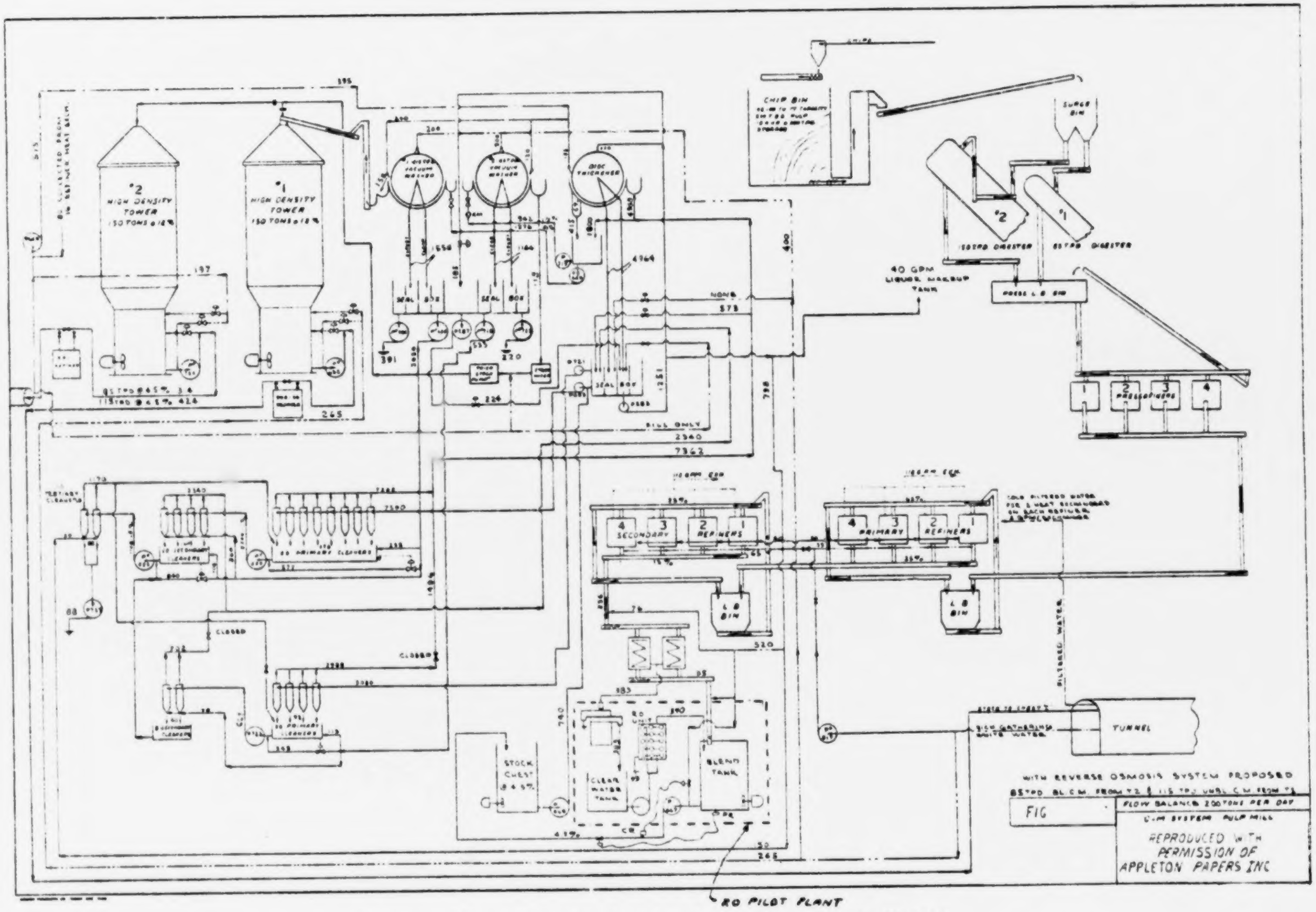

#2 HIGH DENSITY TOWER 150 TONS @ 12%
#1 HIGH DENSITY TOWER 150 TONS @ 12%
85TPD @ 4.5% 3.6
115TPD @ 4.5% 4.26
265
197
195
515
DISC THICKENER
SEAL BOX
SEAL BOX
SEAL BOX
391
220
224
1656
1164
4764
1251
BILL ONLY
2340
7362
NONE
573
400
798
CHIP BIN
CHIPS
SURGE BIN
#2
#1
150TPD DIGESTER
85TPD DIGESTER
40 GPM LIQUOR MAKEUP TANK
PRESS L.B. BIN
1
2 PRESSAFINERS
3
4
4 SECONDARY
3
2 REFINERS
1
4 PRIMARY
3
2 REFINERS
1
L.B BIN
L.B BIN
520
FILTERED WATER
TUNNEL
RO UNIT
CLEAR WATER TANK
BLEND TANK
STOCK CHEST @ 4.5%
740
50
265
TERTIARY CLEANERS
88
PRIMARY CLEANERS
SECONDARY CLEANERS
CLOSED
CLOSED
WITH REVERSE OSMOSIS SYSTEM PROPOSED
85TPD BL.C.M. FROM #2 & 115 TPD UNBL C.M. FROM #1
FIG
FLOW BALANCE 200TONS PER DAY
C-M SYSTEM PULP MILL
REPRODUCED WITH PERMISSION OF APPLETON PAPERS INC
RO PILOT PLANT

Figure 37. Chemimechanical Pulping Flow Sheet

pressure might alter this preliminary conclusion substantially and thereby reduce evaporation costs.

Dewatering of the high consistency pulp coming from the secondary refiners seemed a logical approach to the problem of isolating the wash waters in the smallest practical volume. At this point the high consistency pulp contained a relatively large portion of the total pollution load from the pulp mill. Several samples of wash water, which had been hand pressed from the high consistency pulp available from the blend tank at this point in the pulp washing system, confirmed these preliminary conclusions. For the purpose of conducting this field demonstration, provision was made for setting up a Zenith screw press previously used in the old deinking mill which had been shut down and dismantled when the new chemimechanical pulp mill was placed in operation.

The press waters from the Zenith Press were found to have a temperature range of 65-70°C and a pH range of 7.5-8.2. The temperature was adjusted for membrane concentration processing to 40-45°C and the pH range to 6.0-7.0. The feed liquor contained relatively large amounts of partially solubilized material in the form of fine colloidal particulate organics, and at times the concentration of these fines were as high as 25 percent of the total solids (or 1.5 g/l in 6 g/l total solids). The presence of these fine hydrocolloids in the feed liquor could be of special concern in designing a concentration and disposal system free of fouling and plugging problems.

After installation of the Zenith screw press, a sampling program was undertaken for the purpose of evaluating the efficiency of this method of dewatering the high consistency pulp. The analytical data from two sets of samples are summarized in Table 71, together with the results of calculations to determine recovery efficiency in terms of solids, COD, BOD_5, sodium and volatile acids (as acetic).

The data presented in the table derive from the analysis of solutes recovered in the pressate from two runs at different press settings. The press cake of moist pulp fiber from each run was then subjected to controlled laboratory washing by filtration of the reslurried 7 percent consistency pulp through Eaton Dikeman No. 615 filter paper. The filtrate from the first wash corresponded to the effluent from the normal mill washing step. The total of the solutes contained in the pressate, plus the solutes in the first stage wash, provided a measure of the total pollution load discharged from existing washing practices within this mill. A second washing through a lab filter, after again reslurrying the fiber pulp to 7 percent consistency, provided a measure of the solutes remaining in the pulp as it leaves the pulp mill for production of paper. The total of the solutes in the pressate, plus that in Filtrates I and II, provide a measure of the total solutes fed to the press. The press efficiency could then be calculated in terms of the percentage of solutes actually recovered by the press from the total of the solutes normally removed in the total washing operation (Pressate + Filtrate I).

TABLE 71

CALCULATION OF PRESS EFFICIENCY FOR COLLECTING CM WASH WATER SOLUTES

Basis: 1 Gram of Dry Pulp

Feed to the Zenith Press = 13.28 grams water
Cake from the Zenith Press = 1.86 grams water
Pressate from the Zenith Press = 11.42 grams water = 0.011 liters water (assuming a specific gravity of pressate = 1.0)

	Milligrams per Gram of Dry Pulp					
Constituent	Pressate	I Filtrate	II Filtrate	Solutes Removed in Wash	Total Solutes to Press	Press Efficiency,[a] percent
Set No. 1						
Total solids	65.5	12.7	6.3	78.2	84.5	77.5
COD	77.4	16.0	8.2	93.4	101.6	76.1
BOD	22.4	4.0	1.9	26.4	28.3	79.1
Sodium	8.7	1.7	0.9	10.4	11.3	77.0
Volatile acid	19.0	3.7	2.3	22.7	25.0	76.0
Set No. 2						
Total solids	80.6	9.9	4.9	90.5	95.4	84.5
COD	82.5	11.4	6.6	93.9	100.5	82.0
BOD_5	30.6	3.1	1.8	33.7	35.5	86.2
Sodium	5.4	1.2	0.6	6.6	7.2	75.0
Volatile acid	21.2	4.1	2.9	25.3	28.2	75.1

[a] Press efficiency, percent = (Solutes in the pressate/total solutes fed to the press) X 100

Attainment of the desired level of liquor collection at 80 percent recovery seemed to be well established from these tests on samples obtained in sustained operation with use of commercially available press equipment. Furthermore, some initial concern over the effect of a screw press operation on pulp fiber quality was apparently without foundation. However, the mill technical staff felt the recovery problem would be better taken care of with even higher levels of efficiency and fiber quality using more modern dewatering equipment.

The mechanical stresses of the screw press apparently did bring about a side problem experienced with the actual operation of the press. This was concerned with the apparent increase in the content of colloidal organics in the pressate. It was suspected that the screw press served to remove a substantial amount of the colloidal material from the fiber which might result from hydrating and removing polysaccharides in a colloidal form. This problem along with its effect on the membrane performance is again referred in more detail in later discussion of the data for this field demonstration.

Availability of the screw press, together with its installation and testing by the mill staff, greatly accelerated progress in undertaking and executing this RO field demonstration.

PROGRAM AND DATA OF THE FIFTH FIELD DEMONSTRATION

Equipment

Small pilot RO equipment, similar to that used for processing bleach effluents in the fourth demonstration, was considered best adapted for conduct of this field trial. Volume production of reliable membrane modules suitable for re-equipping the large trailer unit had not been proven in the intervening months since completing the third field demonstration, although the large unit remained in continuing operation for developing engineering design data, with the less than reliable supply of rebuilt modules delivered in September, 1968. Smaller numbers of newly improved tubular modules were available from development operations at Calgon-Havens and were used in this trial. A duplex pump unit, a module test stand complete with automated controls, plus temperature controlling equipment with a tubular heat exchanger and pH control equipment, were moved into the mill and connected to the feed supply system based on the Zenith Press installed by the mill staff, see photo, Fig. 66 (Appendix C). A field engineer from the Institute staff supervised installation and maintained the unit in operation, with a careful program of daily sampling. Most of the analytical control studies were carried out in the Institute laboratory a few miles away.

A flow sheet provided in Fig. 38 provides a schematic presentation of the various unit operations of pulping, pulp refining and washing, liquor collection, and of RO concentration processing of the pulp wash water after cooling and pH adjustment. The pulp slurry from the blend tank after the secondary refiners was dewatered in the Zenith Press as previously described. The pressate flow at about 40 gallons per minute was screened through a Sweco vibrating screen of 100 mesh, and then was pumped to the main storage tank having a capacity of 5000 gallons, sufficient for 12 to 14 hours of operation for the RO unit. The tank was filled twice daily from short 2 to 3-hour runs of the press. Feed liquor from the storage tank was cooled to 40 to 45°C by passing through the tubular heat exchanger, and the pH was then adjusted to less than 7.0, with dilute sulfuric acid in an agitated 50-gallon mix tank. Overflow from the mix tank passed to the 50-gallon

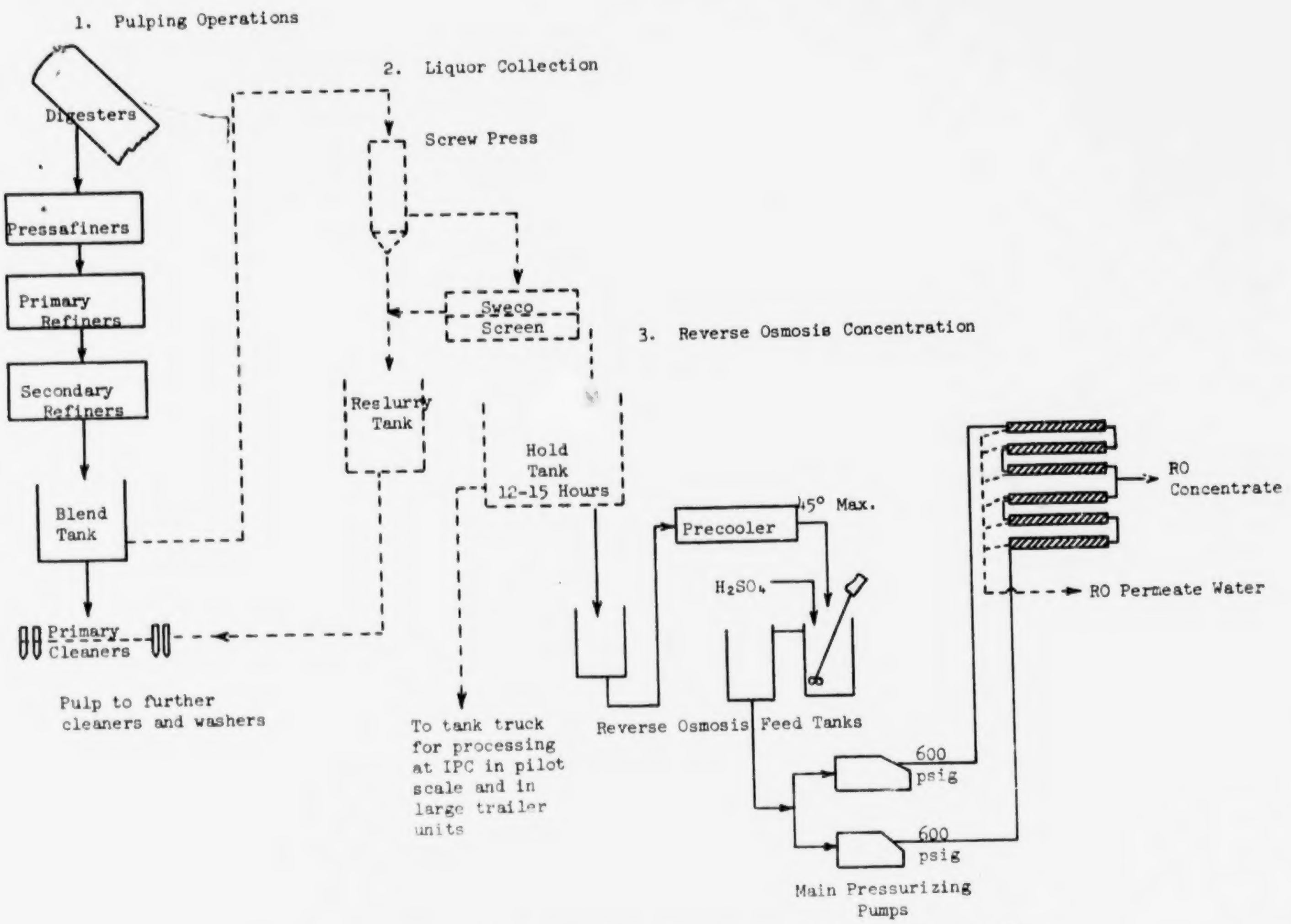

1. Pulping Operations
Digesters
Pressafiners
Primary Refiners
Secondary Refiners
Blend Tank
Primary Cleaners
Pulp to further cleaners and washers
2. Liquor Collection
Screw Press
Sweco Screen
Reslurry Tank
Hold Tank 12-15 Hours
To tank truck for processing at IPC in pilot scale and in large trailer units
3. Reverse Osmosis Concentration
Precooler
45° Max.
H₂SO₄
Reverse Osmosis Feed Tanks
600 psig
600 psig
Main Pressurizing Pumps
RO Concentrate
RO Permeate Water

Figure 38. Schematic of Reverse Osmosis at Appleton Papers Inc.

RO feed tank and then to the Duplex Milton Roy pressurizing pump feeding directly to the RO system. Each of the individual piston pumps in the duplex pumping unit fed a separate, parallel bank of three 18-tube Calgon-Havens modules. The modules were manufactured and delivered during the early Spring months of 1971. The pump unit and module test stand, with automated controls, have been previously described. The conductivity of the feed solution was monitored by a Foxboro dynalog conductivity recording unit, as a continuous indication of the sodium and indirectly of the solids content of the wash water being processed.

After the startup it was found necessary to add a slow speed, 70-inch agitator operated by a 5 Hp mixer, to the 5000-gallon storage tank to keep the colloidal floc in suspension.

Data and Results

The experimental program was conducted in two phases. The principal operations with the pilot unit located at the mill comprised Phase I and were directed to establishing a continuous, straight-through processing of the dilute feed liquor to establish operating parameters on a sustained basis. It was not possible to concentrate to 10 percent solids with the small unit operated in that manner. However, on occasion when the feed liquor supply was interrupted by pulp mill shutdowns, several short concentrating runs were conducted at the mill by operating the unit on a recycle pattern rather than straight through.

Phase II studies to further establish operating methods and data for the higher levels of concentration to 10 percent solids were conducted with small and large units located at the Institute in Appleton using feed liquor supplies trucked from the mill.

Phase I RO Pilot Operations at the Mill

The RO unit at the mill was operated continuously in so far as possible around the clock and through the weekends for the six-week period from May 12, 1971 through June 30, 1971. However, the liquor supply was interrupted at times by mill shutdowns. Brief 2 to 4-hour shutdowns for module washups occurred at the end of each run. Under these conditions, eleven runs were completed at the mill, for which analytical data on membrane performance and rejections are summarized in Table 72, and flux rate performance is shown in Fig. 39.

As the experimental program developed, a pattern of operating problems developed in two chief categories. A serious loss in flux rates was encountered as concentration of the wash waters advanced toward the 10 percent solids level. Advancing the velocity of flow through the tubular modules helped, but provided only a partial answer to the reduced flux rates. The first area for substantial improvement developed late in the study of concentrating problems after it became apparent that the osmotic pressure was quite high in this type of pulping effluent due to the content of Na_2SO_4. The osmotic pressure, which advanced

TABLF 72

RO PERFORMANCE WHILE PROCESSING CHEMIMECHANICAL PULP WASH WATERS

Run	1A	1B	2	3	4	5	6	7	8	9	10A	10B	10C	11
Solids, mg/l														
Feed	5062	14,854	8568	14,150	5718	6367	6377	13,270	11,960	6630	4613	19,710	41,175	6188
Permeate	104	221	64		97	118	270	170	140	245	292	935	410	234
Rej., percent	97.9	98.6	99.2		98.3	98.1	95.8	98.7	98.8	96.3	93.7	95.2	99.0	96.2
BOD_5, mg/l														
Feed	1445		3058		1670	2216	1487	3240	6010	1110	3060	6095	17,700	2548
Permeate	56		32		46	56	141	112	38	118	196	232	134	103
Rej., percent	96.1		99.0		97.2	97.5	90.5	96.5	99.4	89.4	93.6	96.2	99.2	96.0
COD, mg/l														
Feed	5830		13850		6660	7115	7417	15,620	13,730	7400	10345	10,975	45,200	7373
Permeate	159		126		144	143	269	229	154	228	400	699	356	264
Rej., percent	97.3		99.1		97.8	98.0	96.4	98.5	98.9	96.9	96.1	93.6	99.2	96.4
Sodium, mg/l														
Feed	1372		743		752	868	886	1643	1550	894	1288	2740	5270	765
Permeate	20		16		17	24	62	59	38	53	107	204	98	56
Rej., percent	98.5		97.8		97.7	97.2	93.0	96.4	97.6	94.1	91.7	92.6	98.1	92.7
VOA, mg/l														
Feed	1448	3654	2380		1260	1440	1474	3127	2844	1830	2646	4417	9240	1429
Permeate	59	92	36		22	63	181	142	249	152	226	376	218	110
Rej., percent	95.9	97.5	98.5		98.2	95.6	87.7	95.4	91.2	91 7	91.5	91.5	97.6	92.3
Optical Density at 281 nm														
Permeate	0.545	1.06	0.507		0.775	0.795	1.423	0.933	0.697	0.848	1.400	2.105	1.20	1.17
pH														
Feed	6.7	6.6	6.7	6.5	6.6	6.8	6.7	6.5	6.5	7.3	6.2	6.2	6.6	6.4
Permeate	6.1	6.1	6.2		6.2	6.1	6.5	6.6	7.1	6.9	6.5	6.6	6.5	6.6
Temperature, °C	35.2	36.0	36.4	37.5	42.2	38.2	42.0	43.0	43.9	41.1	35.0	35.0	38.9	41.8
Pressure, psig														
in	610	600	600	600	600	600	600	700	600	590	700	700	700	600
out	555	445	465	460	460	460	455	545	450	455	555	550	550	470
Velocity, ft/sec	2.9	4.45	4.45	4.45	4.55	4.55	4.55	4.55	4.55		4.5	4.5	4.5	4.5
Flux, gfd @ 40°C	4.7-8.3	2.3	2.9-6.0	2.7	6.0	4.8-6.0	4.5-6.6	1.8-2.5	1.9	3.3	5.2	3.1-5.2	1.3-2.0	2.8-6.4
Time, hours	13	35	186	44	50	108	134	22	23	31	63	6	3	54

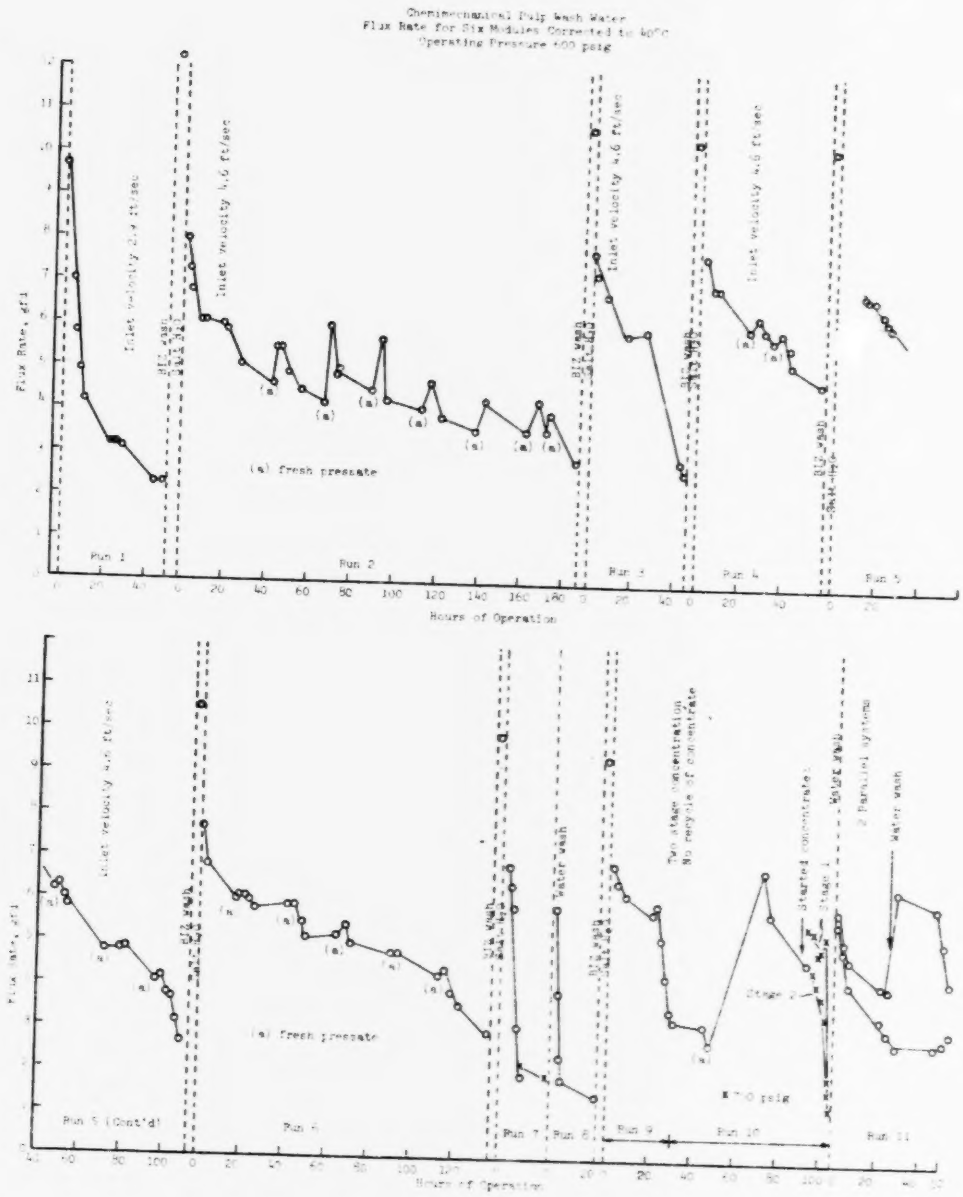


Figure 39. Flux Rate History While Processing with RO Small Unit

above 500 psig in the concentrate, substantially reduced and nearly eliminated the effective driving force of the RO system operating pressure at 600 psig when processing at the higher levels of concentration. Higher operating pressures to 800 psig could be expected to effectively answer this part of the problem.

A second problem more difficult to evaluate became increasingly apparent as the project advanced. Fouling of the membrane by colloidal organics in the feed was observed to increase with operating time and varied with the age of the feed liquor. Development of a colloidal floc was observed during a few hours of holding in the 5000-gallon feed tank. Installation of a slow speed agitator to keep the floc in suspension noticeably improved the flux rate performance. However, freshly prepared liquor was more easily processed at the mill with less fouling than aged liquor. The aging effect and fouling with reduced flux rates were even more apparent in liquor hauled to the laboratory where the fouling problem further increased with holding time. A search was conducted for evidence of a hydrating reaction on the polysaccharide-derived colloids, and indications pointed to probable increase in the content of hydrocolloids. Minimizing the holding and processing time of the feed liquor to reduce the postulated hydration reactions, seemed to be the most promising route to maintaining high flux rates during concentration after allowing for the osmotic pressure problem.

A detailed description of the eleven experimental runs conducted over the six-week period of operation for Phase I at the mill follows.

Each of the eleven runs of from 10 hours to one-week duration (Table 72) was followed by a washup with BIZ detergent, and in all cases the flux rate was restored, in terms of a control test with NaCl solution, and in the initial rates of flux for the next run on wash water feed. It will be noted that Runs 7, 8, and 10 were exclusively operated as concentrating runs with recycle of the concentrate, and Runs 1 and 3 were also concluded with brief concentrating runs on recycle.

Run No. 1

The first run was conducted first for 13 hours on a continuous, straight-through feeding operation, with feed liquor having an initial solids concentration of 4.2 g/l and increasing to 6.1 g/l. The flux rate dropped from 9.7 gfd to 4.5 gfd in the first 7 hours of operation. The velocity was advanced to 4.5 ft/sec from the starting rate of 2.9 ft/sec at 24 hours when the flux rate had decreased to 3.1 gfd, but with only a slight improvement to be noticed in the flux rate. A concentrating trial on recycle was undertaken as Run 1b at the 27th hour, and continued for 8 hours with a further drop in flux rate to 2.3 gfd. The operating pressures were 600 psig at the inlet and from 555 psig at outlet in Run 1a to 445 psig in Run 1b. Rejections for both 1a and 1b runs were excellent at levels well above 95 percent for all categories measured, including BOD_5. It was apparent that increasing the velocity failed to improve the flux rate significantly once the membrane had been substantially fouled.

Run No. 2

Sustained operation was carried out for 189 hours in the second run. An inlet velocity of 4.5 ft/sec was maintained, which controlled much of the loss in flux rate observed early in the first run. Each batch of fresh feed from the press produced an immediate improvement in flux rate. This flux improvement was temporary for a period of only a few hours, but provided evidence for a liquor aging reaction, with apparent production of a colloidal floc capable of fouling the membrane. The floc could readily be observed during formation and settling in the large storage tank. Its formation could not be prevented, but installation and use of the slow speed agitator in midrun served to keep the floc in suspension with some improvement apparent in the flux rate.

Operation was continued through the weekend, but the supply of feed wash water was limited, and to maintain operation the velocity of flow had to be decreased to 3.8 ft/sec. The flux rate dropped off steadily with the reduced velocity, and continued a steady decline for the next four days, after which the unit was shut down and given a BIZ detergent washup. The flux rate on water and on 0.5 percent NaCl test solution was apparently restored fully by the washup.

Pressure pulsing which had alleviated fouling problems with the NSSC liquor in the second field demonstration had no apparent affect on the fouling produced in processing the high-yield chemimechanical (CM) pulping wash water. Various pulsing schedules were tried for 1-minute periods each hour to 3 hours, without apparent effect when the velocity of flow was maintained above 2.5 ft/sec.

Run No. 3

A new start with dilute wash water feed in a continuous, straight-through study of flux rates, with pressure pulsing and storage tank agitation, was established, but the supply of feed liquor failed at 26 hours after a shutdown for motor trouble in the pulp mill. The unit was converted to recycle operation for concentration and reached a level of 14.1 g/l solids after 19 hours. The flux rate dropped steadily from 5.95 gfd to 2.7 gfd. The run was terminated at 37 hours and the unit given a BIZ detergent washup, which again restored the water and NaCl flux rates to a normal level of 8.0 gfd. Fouling appeared to be the chief factor causing the reduction in flux rate.

Runs No. 4, 5, and 6

Three successive runs followed. On each of these the periods of achieving flux rates sustained above 4.5 gfd were of increasing duration. These were conducted with continuous, straight-through operation utilizing agitation in the storage tank and pressure pulsing with velocities maintained at 4.55 ft/sec, and with inlet pressure at 600 psig. Agitation was added to the small feed storage tank in Run 4, but the runs were in other ways conducted by methods similar to that in Run No. 2. Run 4 continued for 50 hours before the flux rate dropped below the 4.5 gfd level. Run 5 held the flux for 100 hours and Run 6 for 120 hours before reaching the 4.5 gfd level. Each of these runs was terminated with BIZ detergent washups, which restored the fresh water and NaCl test water flux rates to the original level. The curve for the falling flux rate was steeper on this wash water than for all other pulping effluents tested in this project, with the exception of kraft pulping rewash water. But indications in these test runs pointed to capabilities for maintaining continuous operation on dilute feed at rates above 4.5 gfd for practical periods of several days to a week or more between short period washups.

A minor problem occurred in acidifying the feed for early stages of Run 6. The analytical data show somewhat lower rejections, ranging below the usual 95-99 percent level to the 88-95 percent level. Apparently, some sodium acetate was hydrolyzed by the excess acid to release free acetic acid which then passed through the membrane and was lost in the permeate.

Runs 9 and 11

Two additional runs on dilute feed liquor with straight-through operation were carried out with a modified hookup for the two banks of modules to put the second bank in series after the first bank instead of two banks in parallel. The low level of feed concentration in the first bank was a minor factor in evaluating the results, which tended to further verify the picture for early stage concentration of the wash water at moderate flux rates.

Five brief runs (1b, 3, 7, 8, and 10) were conducted at the mill as preliminary trials of concentration to higher levels reaching toward the goal of 10 percent solids concentration. All were conducted with recycle, since concentration was not possible on a straight-through operation with the limited equipment at hand. The flux rate dropped precipitously on all trials, with advancing levels of concentration approaching 5 percent solids and higher. The flux rate was shown to be readily restored by washing, and experiments indicated the wash with BIZ detergent might be unnecessary. Warm water seemed sufficient to restore the flux to nearly the original value for routine operation, although the BIZ washup still seemed advantageous for close experimental control of membrane performance in experimental studies.

Run 11 was made to compare the performance of Banks 1 and 2 under different conditions of washing after substantial fouling occurred. In both cases the initial flux rates at 5.6 and 5.8 gfd decreased over a period of 24 hours to 4.1 gfd. Bank 1 was then washed with water which brought the flux rate back to 6.4 gfd. Bank 2 was not washed and the flux continued to drop from 4.1 to 2.8 on the second day of operation. Operation continued for another day and the flux rate for Bank 1 dropped at much slower rates of fouling to 4.25 gfd.

Runs 7 and 8 were brief concentrating runs starting with feed liquor aged for less than one day. In each case the starting flux rate after a washup was 7 gfd. In Run 7 the concentration during recycle increased from about 6 g/l solids to 14 g/l, and for Run 8 the concentration reached 12 g/l. For Run 7 the operating inlet pressure was maintained at 700 psig. The flux rate dropped to 1.8 in one bank and to 2.5 in the second bank for an average of 2.2 gfd. In Run 8 the inlet pressure was 600 psig and the flux rate dropped to an average of 1.9 gfd. Both runs were conducted with a velocity of 4.55 ft/sec. These results were disappointing, but another run at an operating inlet pressure of 700 psig maintained a flux rate of 5.2 gfd for 63 hours at a starting feed concentration of 4.6 g/l solids and which was carried to a concentration of 19.7 g/l. The average flux rate at 5.2 gfd indicated the increased operating pressure might, substantially care for the problem of balancing the rising osmotic pressure as the concentration progressed. The concentrating run was continued in Run 10b for six hours, during which the flux rate was maintained by Bank 1 at 3.1 gfd and at 5.2 gfd in Bank 2. The concentration was then continued to 4.11 g/l in Run 10c for another three hours of recycle operation at 700 psig. The flux rate dropped to 1.3 in Bank 1 and 2.0 in Bank 2.

These concentrating runs were apparently greatly handicapped by the growing evidence for development of a fouling agent, probably in the nature of a hydrocolloid of polysaccharide origin as a time-based reaction or aging effect during the recycle operations. It was apparent in the straight-through operations that fresh liquor had an aging effect in a period as short as 2-4 hours after passing through the screw press. These concentrating runs were necessarily carried out by recycle for substantially greater periods of time, ranging above 20 hours to achieve concentrations approaching 5 percent solids.

It is indeed disappointing that equipment could not be made available for concentration runs on a straight-through type of operation, employing a minimum of recycle with freshly prepared liquor. The holding time for these concentrating runs on a straight-through flow system would be expected to be on the order of 30 minutes or less in commercial operations. These runs provided growing evidence that development of hydrocolloids or gels occurs in this type of spent liquor, and especially after a dewatering treatment through a screw press.

Additionally, the screw press may have inherent a disadvantage in the high pressures, and the resultant stresses and abrasion of the fiber. Such action may serve to remove hydrocolloids which would otherwise remain bound to the pulp fiber by other methods of less vigorous dewatering known to be commercially available for this type of operation. There was considerable evidence that the fouling effect and the aging effect varied to some extent from sample to sample of the press liquor. This could be further evidence that the aging effect and the fouling may be substantially reduced by employing more suitable methods of dewatering the high consistency pulp produced by this chemimechanical (CM) pulping process.

Continuing Study of Methods for Concentrating Above 5 Percent Solids

The problem of developing satisfactory methods of RO concentration of the CM wash water at solids levels above 5 percent were not being satisfactorily solved with the RO equipment installed at the mill. Concurrent studies were undertaken with small and large equipment available at the Appleton facilities of The Institute of Paper Chemistry. Fifty-gallon samples of fresh press water ranging about 5 to 7 grams solids per liter were collected and conveyed from the mill with the least delay en route. These press waters were promptly concentrated about 10 to 15 times by reverse osmosis, under recycling conditions, to remove 90 to 94 percent of the water, and thus achieving 8 to 11 percent total solids in the final concentrate. A final reverse osmosis product at that range of concentration could feasibly be used as feed to a standard evaporation system.

Unfortunately, we could not concentrate large volumes of the pressate at sustained and reasonable levels of flux rates with minimum of recycling under the desired conditions of operation in the large trailer unit. Reactions on aging of the pressate apparently produced excessive quantities of colloidal gels when truck loads of the pressate were stored more than 20 hours in our 5000-gallon feed tank. However, we did have reasonably high flux rates for smaller drum quantities of fresh pressate, for which aging was limited to not more than 15 to 20 hours during transport, storage, and processing. In order to overcome this limitation, 50-gallon samples of fresh pressafiner liquors were collected daily from the mill at about 6 to 7 percent solids concentrations and were further concentrated by reverse osmosis to about 8 to 9 percent solids. Fresh pressafiner liquors showed relatively less fouling of the membrane and their flux rates were somewhat better even when the osmotic pressure reached 500 psia at higher concentrations of the liquors.

For this study, we used the latest Mark III design of Ps-series 18-tube Calgon-Havens modules with No. 310 membranes. The following paragraphs deal with studies on concentration runs conducted on these samples of press and digester liquors.

Osmotic Pressures of Chemimechanical (CM) Pressate and Digester Liquors

One of the first objectives was to determine the effective driving force for different concentrations of the pressates. The flux rate at any concentration of the liquor is directly related to the osmotic pressure of the liquor. This pressure increases as the salt concentration increases during RO processing. The higher the osmotic pressure of the liquor, the lower the flux rate for a fixed operating pressure.

The dilute samples of the pressate were concentrated from 0.7 to 0.8 percent solids by RO, whereas the digester liquors were concentrated from 7.0 to 10.0 percent solids. During these concentration runs, feed, concentrate, and product samples were taken. These samples were analyzed for solids and osmotic pressure. A Vapor Pressure Osmometer (VPO), which operates on the principle of lowering of the vapor pressure, was used to measure the osmotic pressure of each sample of the liquor. An NaCl solution was used as a reference for the VPO.

Figure 40 plots the osmotic pressures versus total solids for pressate and press liquors. It is apparent from this curve that the osmotic pressures for press liquors were high as compared to those for the pressates, and increased linearly from 355 psia at 65 g/l to 450 psia at 100 g/l. Apparently, there were more low molecular weight inorganic materials, especially Na_2SO_4, present in the pressafiner liquors. The osmotic pressures of the press waters also increased linearly with the concentration, but were less than 300 psia for liquor solids concentrations up to 10 percent solids.

Figure 41 gives the specific gravity of the liquor at 20°C for various concentrations of pressate and provides a quick method of estimating the solids content for use in controlling the RO processing of the pressate waters.

Flux Rates and Rejection Ratios During Concentration Runs of Fresh Press Liquors

Two concentration runs were made with 50-gallon samples of fresh liquor using one module at 40°C and 680 psig average pressure. The press liquor, as received from the mill, had 5 to 7 g/l total solids, and the average of the amounts of suspended solids in these pressates varied between 20 and 25 percent of the total solids. In one concentration, the pressate was processed without removing suspended material, whereas for the second concentration run the pressate was centrifuged in a Sharples super centrifuge before RO to remove as much as possible of the floc forming colloidal suspensoids. Higher velocities on the order of 4.6 feet per second were maintained throughout these concentration runs on liquor pretreated to minimize concentration polarization and fouling effects. During the concentration runs, feed, concentrate, and product samples were taken. These samples were analyzed for total solids, sodium, volatile organic acids, BOD_5, and COD.

Figure 42 plots flux rate versus concentration of the liquor for centrifuged and noncentrifuged pressates. The flux rates for noncentrifuged pressate decreased from 8.2 gfd at 7 g/l to 3.2 gfd at 107 g/l, whereas for the centrifuged pressate the flux rates are somewhat higher at all concentrations. An exception was apparent at 76 g/l solids, at which level the flux dropped to 1.5 gfd. This low flux rate may have been due to the aging effect of the liquor at 33 hours for the centrifuged pressate as compared to 22 hours for noncentrifuged pressate. In addition, the flux rates of both centrifuged and noncentrifuged

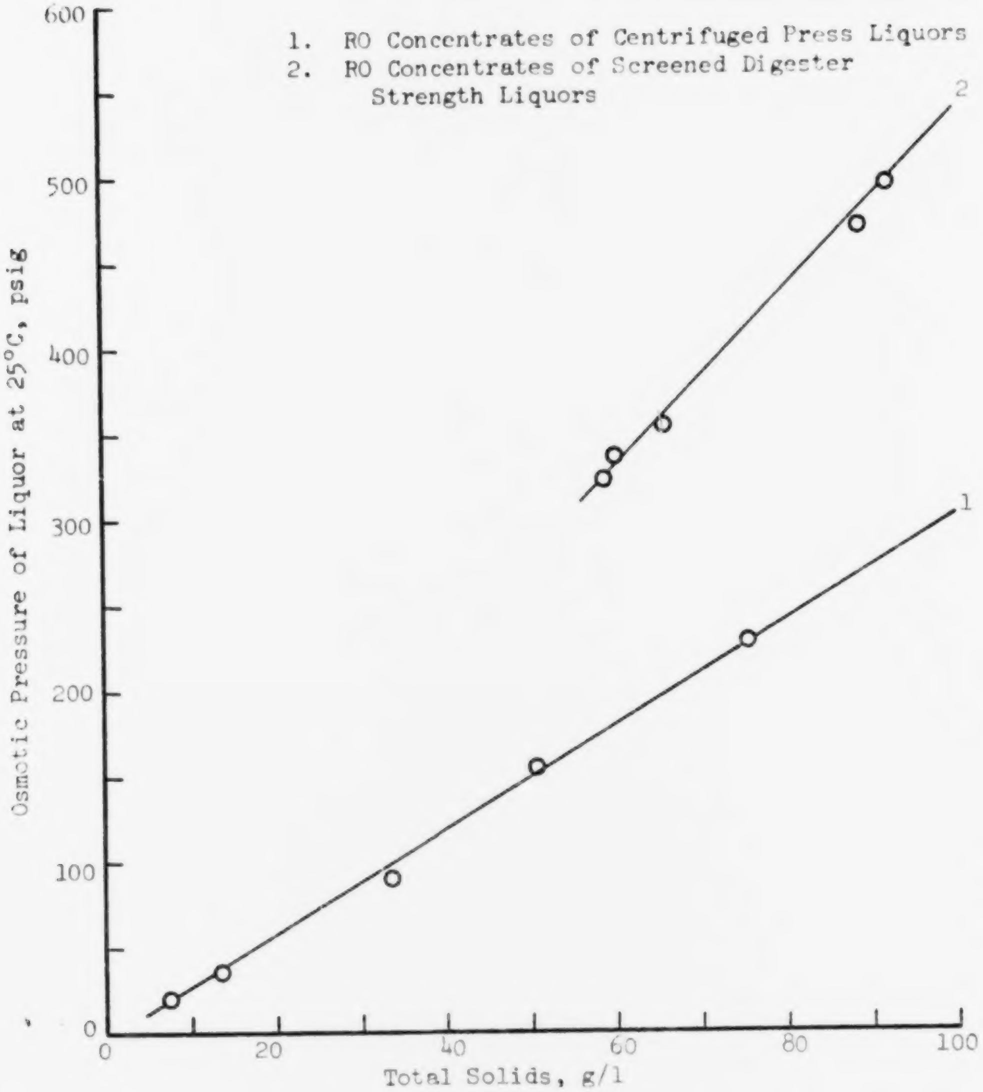


Figure 40. Osmotic Pressure of Pressate and Digester Liquors

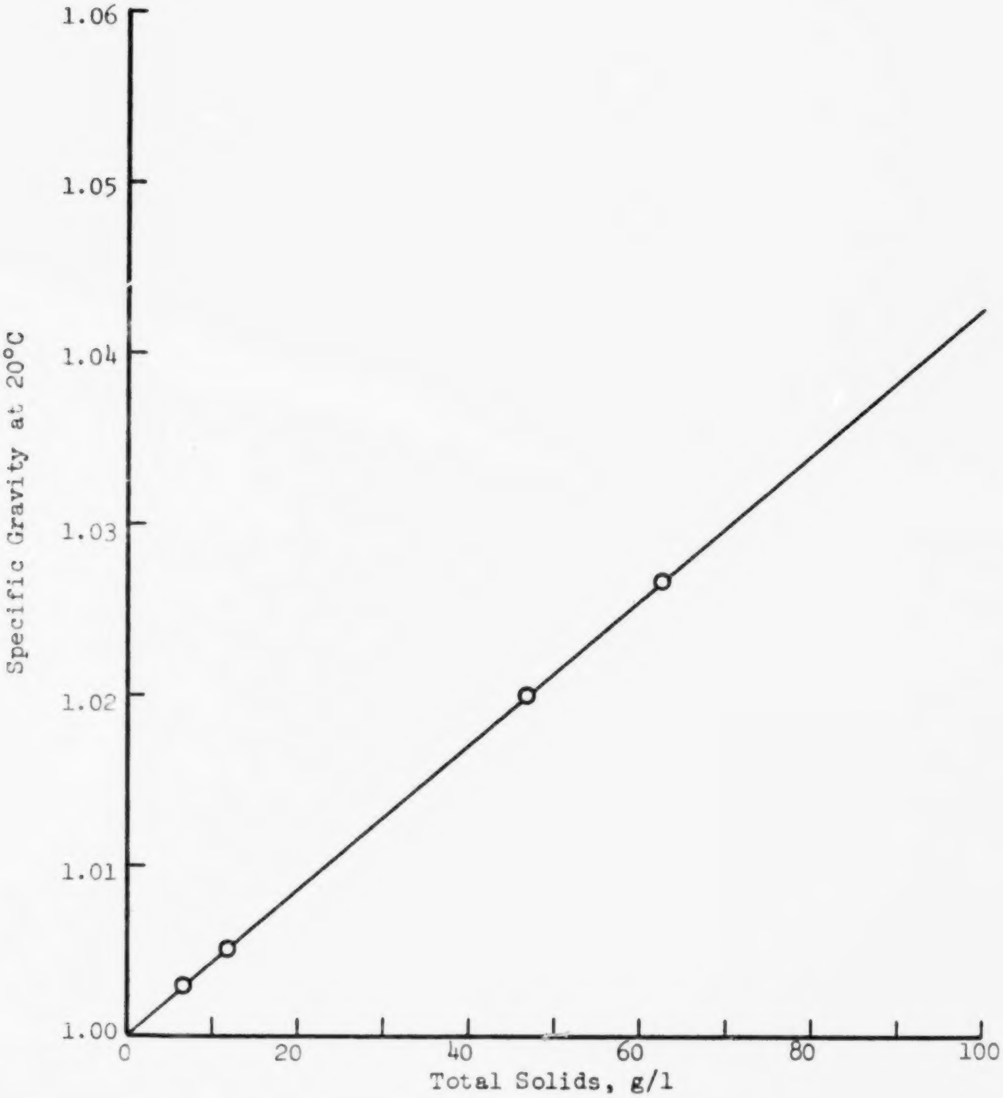


Figure 41. Specific Gravity-Concentration Relationship for Press Liquors

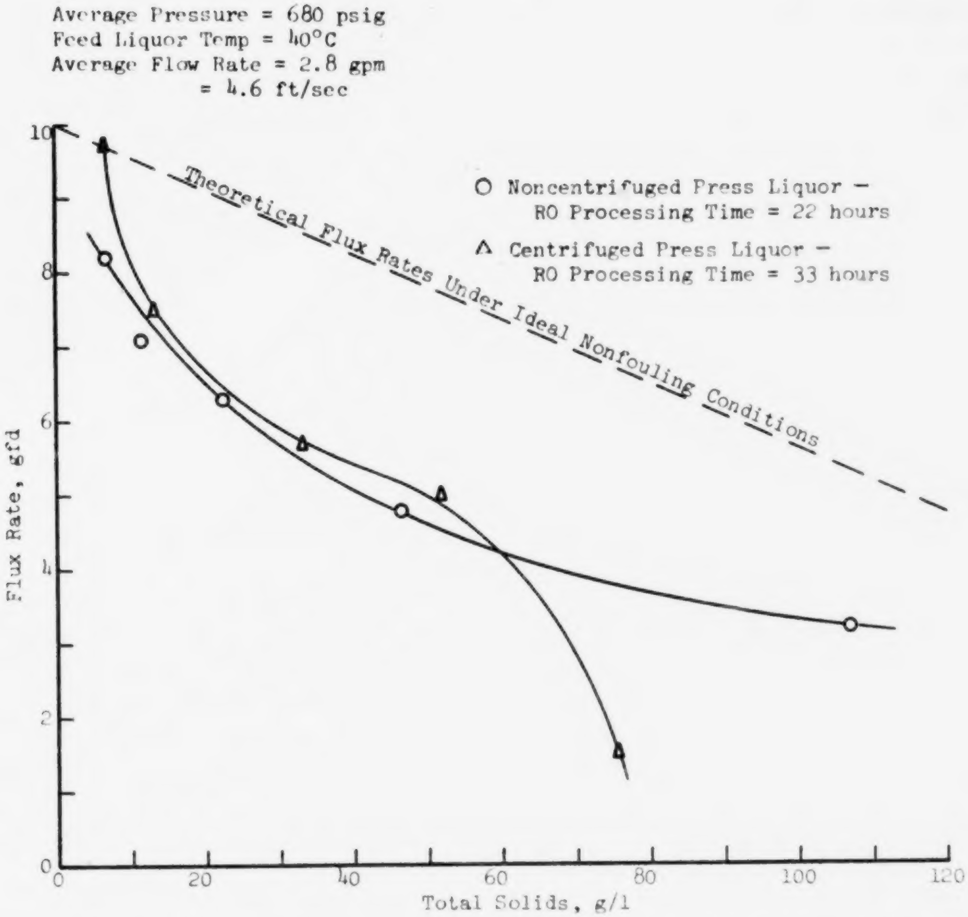


Figure 42. Flux Rates During Concentration Runs with Fresh Press Liquors

pressates are less than the theoretical flux rates as determined from the osmotic pressure under nonfouling conditions. This indicates that there has been constant fouling of the membrane throughout the concentration runs. It was not possible to control this fouling of the membrane even at velocities as high as 7 to 8 feet per second (equivalent to Reynolds Number = 28000-32000). There was some speculation that electrical attraction may have existed between the negatively charged colloids and the cellulose acetate membrane. The literature and small-scale exploratory tests indicate the charge on the membrane is normally negative, but the intensity of this charge is very small. Time was not available for a thorough study of the effect of electrical charges on the fouling of the membrane.

Table 73 lists the flux rates and rejection ratios for both centrifuged and noncentrifuged pressate. The rejection ratios for centrifuged pressate are excellent and range between 95 and 99 percent for all components, whereas for noncentrifuged pressate the rejections vary between 85 and 95 percent. These relatively low rejections in the case of noncentrifuged pressate may have been due to a slightly "leaky" module in this particular run.

TABLE 73

FLUX RATES AND REJECTION RATIOS DURING CONCENTRATION RUNS WITH FRESH PRESS LIQUORS

Average Pressure = 680 psig
Feed Liquor Temperature = 40°C
Average Flow Rate = 2.8 gpm = 4.6 ft/sec

Total Solids, g/l	Flux Rate, gfd	Rejection Ratios, percent				
		Solids	COD	BOD_5	Sodium	VOA
Noncentrifuged Press Liquor (Total RO Processing Time = 22 Hours)						
6.8	8.2	92.7	95.6	--	82.9	91.5
11.8	7.1	93.4	--	--	84.3	--
22.6	6.3	94.2	96.4	--	85.8	87.9
46.6	4.8	94.1	96.7	--	83.3	92.4
107.0	3.2	94.9	--	--	--	--
Centrifuged Press Liquor (Total RO Processing Time = 33 Hours)						
6.8	9.7	98.8	98.7	98.7	96.4	98.5
13.2	7.5	99.3	99.1	99.1	98.8	98.4
33.2	5.7	99.5	99.6	99.6	99.3	98.8
51.8	5.0	99.6	99.6	99.6	99.3	99.5
76.1	1.5	99.7	99.7	99.7	99.4	99.8

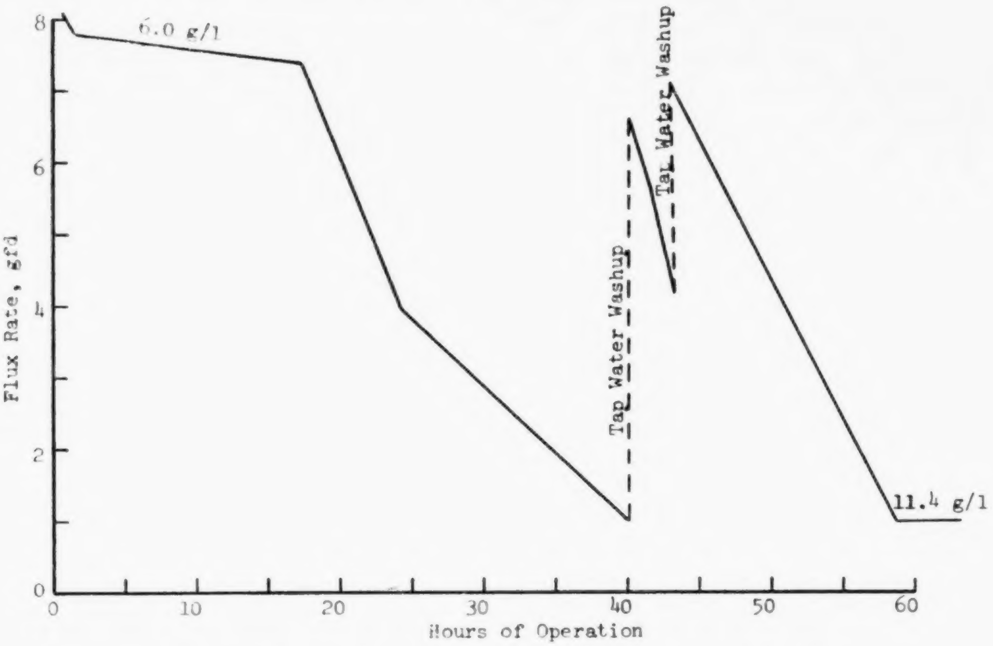
It was also observed that the RO concentrates from noncentrifuged pressate were highly viscous compared to those of centrifuged pressate. The RO concentrate obtained without centrifuging formed a gel at 10.0 percent solids, whereas the pressafiner liquor did not have such a highly viscous character even at 50 percent solids concentration. This gel formation and the viscosity effect led strength to the hypothesis that the screw press may remove a substantial amount of colloidal material following an hydration reaction on the polysaccharides to give the colloidal form. It was interesting to find the viscosity of this 10 percent solids concentrate was greatly reduced at 40 to 45°C temperature. This could promise much less of a fouling problem, if and when membranes become available for operation at temperatures of 45°C and above.

Aging Effect of Press Liquors on Flux Rates and Rejection Ratios

Throughout this study processing difficulties had been observed which seem to be associated with aging of the liquor. Staff chemists working in the field of wood chemistry postulate the probability that hydration of polysaccharides may be taking place in the pressing of the pulp and during aging of the pressate to yield a colloidal form. These hydrated polysaccharides may then be developing some electrical affinity or attraction to the membrane. This affinity of the negatively charged colloids might very well result in severe declines in flux rates, either by increasing the thickness of the membrane or by plugging of the microporous structure.

Figure 43 gives the history of flux rates versus operating hours for centrifuged and noncentrifuged pressates. All the flux rates were measured at 40°C and 675 psig average pressure. Reynolds Numbers as high as 20,000 (equivalent to 4.5 to 5.0 feet per second of velocity in 1/2 inch tube) were maintained throughout the flux rate runs for the purpose of controlling concentration polarization and fouling of the membrane. The data in Fig. 43 indicate the flux rate remains almost constant at 7.5 gfd on relatively fresh noncentrifuged liquors having an age of less than 17 hours. The flux rate decreased rapidly to about 1.0 gfd, with liquors stored longer than 17 hours. As a check, a fresh centrifuged sample of pressate was mixed with a sample aged for 40 hours after centrifuging. This mixture having a solids concentration of 62 g/l was shown to produce a rapid decrease in flux rate to 2.0 gfd during the first 4 hours of RO processing. These experimental studies further confirmed a deleterious effect of aging on flux rates for both centrifuged and noncentrifuged pressates. Centrifuging may remove all or part of the gel-like floc or other suspended material contributing to fouling. If so, it apparently does not bring the aging reaction to a halt and further foulants apparently continue to form. Figure 43 also indicates that the flux rates of both centrifuged and noncentrifuged pressates are restored immediately to their original values each time after tap water flushing of the membrane.

RO Feed = Noncentrifuged Fresh Press Liquor



RO Feed = Centrifuged Fresh Press Liquor, 5.6 g/1
+ Centrifuged 40 Hours Old RO Concentrate, 62 g/1

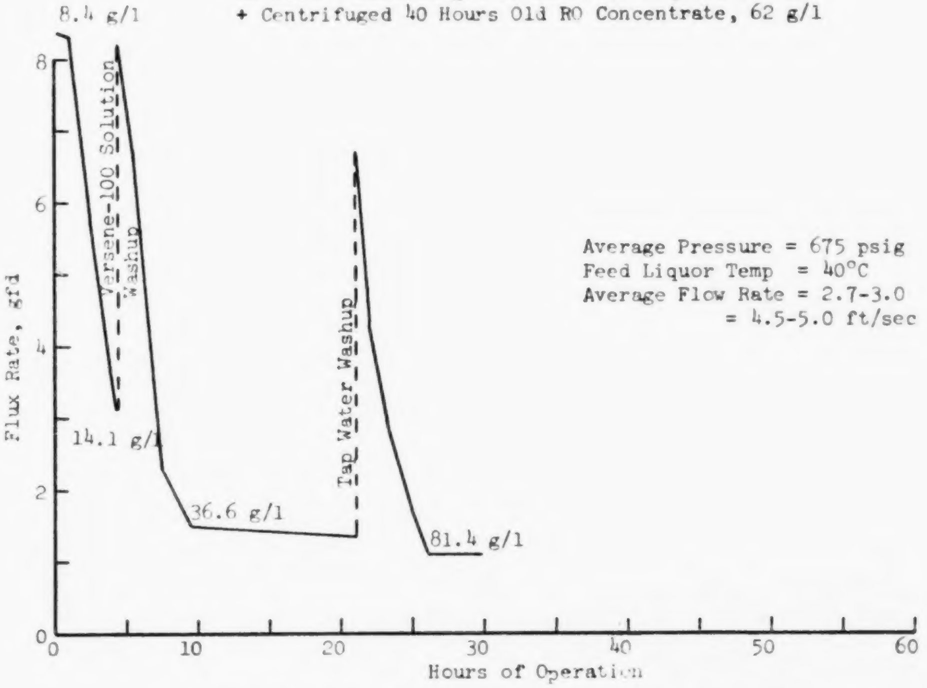


Figure [illegible]. Aging Effect of Press Liquors on Flux Rates

Table 74 shows the effect of aging on pressates in terms of flux rates and rejection ratios. Flux rates decline rapidly with time and with increase in solids concentration. Rejections are rather uniformly high but show a trend toward further improvement as aging progresses. Low starting rejections are known to improve substantially, however. The results of these studies suggest that severe flux rate declines, associated with the aging effect, may perhaps be due to a buildup of a secondary membrane, such as might be formed by colloidal gels attracted to the surface of the cellulose acetate membrane rather than due to the plugging of the porous membrane. Although compaction of the membrane is well known to affect membrane performance, this did not appear to be significantly involved under the conditions being studied.

TABLE 74

EFFECT OF PRESS LIQUORS AGING ON FLUX RATES AND REJECTION RATIOS

Average Pressure = 675 psig
Feed Liquor Temperature = 40°C
Average Flow Rate = 2.7 gpm = 4.5 ft/sec

Time of Operation, hours	Total Solids, g/l	Flux Rate, gfd	Rejection Ratios, percent				
			Solids	COD	BOD_5	Sodium	VOA
Noncentrifuged Fresh Press Liquor							
2	6.0	7.8	98.0	--	--	97.0	89.9
60	11.4	1.0	98.2	--	--	97.5	--
Centrifuged Fresh Press Liquor and Centrifuged 40 Hours Old RO Concentrate							
1	8.4	8.3	99.6	98.9	--	98.4	--
12	36.6	1.5	99.6	99.4	98.9	99.5	99.8
27.5	81.4	1.1	99.6	99.5	99.4	99.3	99.7

Further study and proving will be required, but it is possible to postulate the aging effect of the liquor, which results in rapid flux rate declines under high levels of recycle and during long holding time for the liquor in process, may become less significant in a large-scale RO unit which operates on a straight-through processing cycle with minimum holding time in process. In a large-scale unit, the feed would be concentrated on a straight-through basis to the desired solids concentration using a large number of modules. The total holding time of the liquor in straight-through processing could be 30 minutes or less and seldom more than one hour even if some recycling may be required to achieve full concentration.

DISCUSSION OF FIFTH FIELD DEMONSTRATION

The exploratory studies conducted during the six-week field trial and in the supporting laboratory evaluation of the problems encountered have served to establish RO as an interesting contender among the alternative methods to be considered for processing the dilute wash water effluents from this chemimechanical pulp mill.

Substantial operational problems and difficulties remain for further study, and practical methods of operation must be developed before it can be known whether commercial-scale installation of an RO membrane concentration system could be a feasible answer to the effluent treatment problems at this mill. However, solid accomplishments derived from this field demonstration of the capabilities for RO and in identification of those problem areas which remain.

A first objective of the study has been concerned with developing a feasible method for recovery of a suitable RO feed liquor containing a major portion of the solubilized and partially solubilized wood components and of the cooking chemical residues contained in minimum volumes of the wash water. The trials of the screw press indicated that dewatering of the high consistency pulp immediately after the secondary refiners does answer these requirements very well. Tests of two settings of the screw press in operation showed 80 percent recovery of the total wash water effluent solids was being readily achieved. Removal of the major portion of the solids at that early stage of refining and washing should substantially reduce water requirements for final stage washing, and should greatly increase possibilities for recycle and reuse of the final stage wash waters.

Such recycle and reuse of the final stage wash waters would pick up the 20 percent of the wash water solids remaining in the wet press cake of pulp leaving the screw press. Recycle of the wash water containing these solids would bring them back to the press for recovery in the next cycle. The mill would then be within reach of total treatment and disposal of all pulping process effluent solids.

The indicated volume and solids concentration relationships for collecting the chemimechanical (CM) wash waters are summarized in Table 75. The table also provides related comparative data on findings from this demonstration and on probable goals for design and operation of a commercial concentrating system. The wash waters from CM pulping are presently discharged to the mill sewer with other dilute flows in about 1,250,000 gallons per day at a solids concentration of 0.1 to 0.2 percent. The indicated flow of wash waters which could be collected for RO processing by pressing the high consistency pulp from the blend tank after the secondary refiners was estimated by the mill engineering staff to be about 550,000 gallons, with 0.5 to 0.6 percent solids at the time of making this study. Further improvement in design and operation of equipment for dewatering the pulp could reduce the volume of the wash water feed to the RO concentrating system to give volumes as low as 200,000 gallons per day and solids concentrations at the 1.0 to 1.2 percent level.

TABLE 75

INDICATED FINDINGS AND GOALS FOR CONCENTRATION OF CM EFFLUENTS

	Present Situation	Indicated Findings this Demonstration	Probable Goals for Mill Installation
Collectible Effluent			
Volume, gal./day	1,250,000	550,000	200,000
Total solids, percent	0.1-0.2	0.5-0.6	1.0-1.2
RO Concentrate			
gal./day	--	50,000 to 75,000	20,000 to 30,000
Total solids, percent	--	5 to 10	7 to 12
Feed Available for Evaporation			
gal./day	40,000[a] to 50,000	90,000[b] to 125,000	60,000[b] to 80,000
RO Flux Rates			
(To concentrate from 1 to 10 percent solids), gfd	--	2.5-7.5	8 to 10

---

[a] Digester liquor volume presently estimated at 43,000 gal./day at 7 percent solids.

[b] Digester liquor plus RO concentrate.

The second principal objective for Demonstration No. 5 on CM pulping wash waters was directed to proving the capability of RO for concentrating this solution of wood-derived organics, which are apparently unstable due to continuing reactivity with residual pulping chemicals.

The data accumulating throughout this run provide much evidence of an aging effect probably due to reactivity in the form of hydration of the polysaccharides. This aging effect becomes apparent within a few hours after collecting the liquor, and progresses actively in the first 24 hours to yield gummy hydrocolloids which have been found to foul the membranes and seriously reduce their performance.

Performance of the RO pilot unit operating in the mill on a straight-through flow shows the fresh pressed liquor could be processed at relatively high rates of flux on the order of 7.5 gfd during the first 4 hours, and at rates above 5 gfd for periods up to 17 or 18 hours of holding time for the feed liquor. Fouling becomes severe after a day of storage.

The materials fouling the membranes were readily removed with a water wash. An enzyme-type detergent added to the water may have accelerated the washing under difficult conditions. No permanent effects on membrane performance were apparent during the 6 weeks of operation in the mill and in studies carried out concurrently at the laboratories in Appleton.

It was especially difficult to conduct sustained concentrating runs at levels above 5 percent solids because of the reactive aging effect leading to severe fouling of the membranes during recycle operations extending beyond 17 hours. Equipment was not available for conducting straight-through concentration runs on liquors which were fresh and more easily processed in the mill. A number of small-scale runs were carried out to the 10 percent solids level in recycle runs of limited duration. These runs provided evidence pointing to probabilities that fresh liquor could be processed continuously to achieve solids concentrations at the 10 percent level with properly designed equipment operating to process liquor with holding times of an hour or less with a minimum of recycle. Operation under such conditions would be normally expected in large-scale commercial equipment. These findings were the basis for further tabulation of indicated findings and goals provided in Table 75.

It should, therefore, be expected that engineering design and plant operation of an RO concentrating system in this chemimechanical pulp mill could be directed to collecting 80 percent or more of the wash water solids in about 200,000 gallons of dewatering effluent. Reverse osmosis concentration would be expected to reduce the volume by a factor of about 10 times to give from 20,000 to 30,000 gallons of intermediate concentrate at 7 to 12 percent solids. This intermediate concentrate could then be combined with about 40,000 to 50,000 gallons of digester effluent at 7 to 10 percent solids to give a final 50 percent solids concentrate readily processed for disposal by combustion or alternately for recovery of pulping chemicals and other possible values.

A number of critical problems require further research and development of engineering design factors before an economically feasible commercial operation can be assured and undertaken.

A module life study was not a part of this demonstration. For the most part new modules were available and used for the 6-week period of study. No major failures occurred and, although one module showed evidence of a slight leak at one of the tube seals and was replaced, this was later proven to be a transient leakage that disappeared and the module was put back into use at a later time. Nevertheless, the extensive module life studies conducted throughout the course of the five demonstrations and extensive laboratory studies for this research and demonstration project all were plagued with module failure problems after a few months of operation and showed the critical nature of the module performance and life expectancy over a desired minimum period of 12 to 24 months life expectancy. This problem was considered to be a responsibility and concern of equipment suppliers in terms of design and of close control of manufacturing operations in fabricating the membrane module equipment. Discussion of the effect of life performance on the economics for application of RO processing of effluents of the pulp and paper industry are the subject for further discussion in Sections IX and X.

Next of importance to the life and performance expectancy of membrane equipment is the practical performance in terms of flux rates of permeate through the large and costly areas of membrane required for processing several hundred thousand gallons of effluent waters daily. This demon- stration has indicated that flux rates on the order of 2.5 to 5.0 gfd might be expected under the conditions of these studies, and that better performance ranging around 7.5 gfd might be expected overall with pro- cessing of freshly prepared feed liquors held for periods of one hour or less when concentrating in the range of 1 percent solids to 10 percent solids. This level of permeation rate has been adequately demonstrated in sustained operations elsewhere in this report as pertaining to mem- branes manufactured in the period 1967 to 1970. It should also be noted that newly improved membranes which have become available during 1971 could double these rates. Rates on the order of 8 to 10 gfd seem to be a likely goal for designing a commercial installation from this point onwards.

Nevertheless, the fouling experienced with the unstable and reactive feed liquors utilized in this demonstration and also those of similar reactivity or instability in the white water neutral sulfite semichem and the rewash waters of kraft pulping all point to need for careful control of processing conditions. Exploratory studies conducted during this trial point to hydration reactions on polysaccharides removed from the pulp as being subject to time-based hydration reactions. There was some evidence that the screw press used in dewatering the pulp to produce the RO feed liquor was probably responsible for abrasion of the lignocellulose fibers, thereby removing more of the reactive polysaccharide material responsible for fouling than might otherwise be expected in more modern and less severe conditions of dewatering of the pulp. Development of better methods of dewatering to reduce the fouling problem is an indicated area for further study. Another engineering design problem is expected to arise within the development of the pulp washing system, should the dewatering step with RO concentration be undertaken. Removal of 80 percent or more of the wash water solids from the high consistency pulp coming from the secondary refiners would greatly reduce the amount of processing required in the final stages of washing the pulp. Reduced volumes of wash water would be required for those final stages. Complete recycle of the resultant dilute wash stage effluents back into the main pulp refining and pulp washing operations could be expected to become a large step toward achieving complete closure of the pulp mill effluent water system. The remaining 20 percent of the solids collected in the initial dewatering step would be recycled into the recovery system. Careful design of the system should go far toward achieving this objective.

Remarkably high levels of rejection by the membrane system have been observed throughout this demonstration study. Recoveries at the level of 95 percent or better might be expected in processing these effluent waters by RO. However, the membrane systems are not perfect and the remaining fraction of 5 percent or less of solids passing into the permeates could present a minor effluent problem if discharged to receiving waters. Use of these relatively clean, reclaimed permeate waters for final stage pulp washing would be another step toward closing the system and achieving complete control of pollution problems in this mill. It was not possible to evaluate the chemical buildup problems which might result from recycle of low molecular weight materials which might be passing through the membrane into these permeate waters during weeks or months of operating a recycle system. Analytical evaluation and study would be indicated as a final step in determining the amount of the recycle of the permeate water which could be tolerated. Nevertheless, it is probable that most if not all of the permeate waters could be recycled to some more tolerant point in the mill system, if not in final stages of washing the pulp.

The remaining sections of this report further develop the possibilities for optimizing the engineering data of an RO concentration system and of evaluating process economics.

SECTION VIII

ENGINEERING AND DEVELOPMENT STUDIES

Engineering Design Factors

The material concerning development of design factors for this project, as detailed on the following pages, has been previously presented in part as a published paper[6].

Prior sections in this series review the development, design, and operation of reverse osmosis equipment for laboratory, pilot, and five large field demonstrations for concentration processing of pulp and paper effluents. Design factors developed in the early phases of these studies were often based upon incomplete analytical characterizations of the wastes and their effect on performance of membrane equipment. The resulting estimations for design purposes proved out remarkably well in setting up the laboratory, pilot, and fairly large field demonstrations at flow rates ranging to 60,000 gallons per day and more. However, areas of need for more exact analytical and design data have become apparent as the trials proceeded and experience with field conditions developed. Particularly, there has been need for more exact data covering changes in processing variables as concentration proceeds in the range of 0.1 percent to 10 percent dissolved solids.

This discussion deals mainly with development of design data on calcium- and ammonium-base acid sulfite, NSSC, and second-stage kraft bleach effluent liquors in the following areas of study:

Determination of Reynolds Numbers.

Pressure drop and pumping energy requirements.

Determination of osmotic pressures.

Determination of rejection ratios.

Product flux rate-temperature relationship for calcium-base acid sulfite liquor.

Effect of velocity on flux rates of Na- and Ca-base liquors.

Microbiological fouling and membrane compaction.

Determination of Reynolds Number

One of the first objectives in these studies was to determine required degrees of turbulence and mixing necessary to minimize concentration polarization and fouling of reverse osmosis membranes. These measurements were developed as Reynolds Number, applicable at various temperatures and concentrations of the different types of pulp liquors. This of the important factors of concern in avoiding membrane "fouling" and for maintaining high flux rates. Concentration polarization produces several effects detrimental to the membrane separation process:

(1) The osmotic pressure that must be overcome is that corresponding to the solids concentration at the membrane surface. This is true, since concentration polarization causes the effective osmotic pressure of the bulk of the solution. For this reason, the required operating pressure for the RO cell is increased by the polarization effect, and the pumping power requirements will also be increased.

(2) The concentration polarization may have a detrimental effect upon the dissolved solids content of the product water because the dissolved solids content of this permeate will increase as the solids concentration at the membrane surface increases.

(3) The deterioration of the membrane may be hastened by increased solids content of the product water, and concentration polarization can aggravate this effect.

(4) Finally, excessive concentration polarization may cause precipitation of solids at the surface of the membrane.

Therefore, it is important to reduce concentration polarization by maintaining turbulent flow across the surface of the membrane. The calculation of Reynolds Number (N_{Re}) as a measure of the degree of turbulence requires the determination of the density and viscosity of the liquor.

The viscosities of the liquor were determined using an Ostwald Viscometer, whereas the specific gravities were determined using a Pycnometer. The pH of each sample of the liquor was adjusted between 4.0-4.5 with sodium hydroxide or sulfuric acid, depending on the initial pH. Then Reynolds Number for different liquors were determined using the experimental values of the densities and viscosities at different temperatures and percentage solids of the liquor. The data for N_{Re} and temperatures are fitted to a straight-line relationship, using the method of least squares at different percentage solids of the liquor.

The results of Reynolds Number for NSSC white water, ammonium-, and calcium-base acid sulfite liquors, and second-stage KBZ liquors, are plotted in Fig. 44-47 at different percentage solids and temperatures of the liquors. Various linear velocities (μ) within the 0.5 inch diameter (D) tubes were tested.

Turbulent flow is considered to occur at Reynolds Number above 4000. From Fig. 44-47 it is apparent that a velocity of about 1.0 foot per

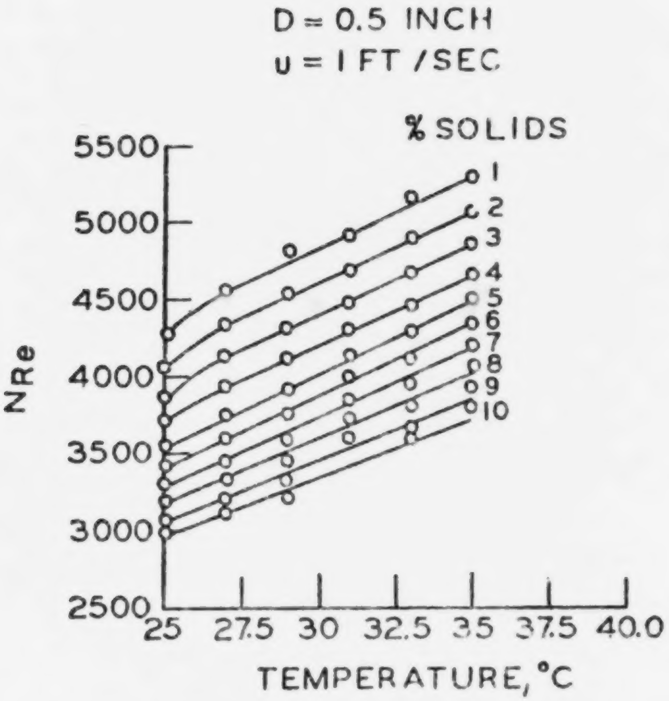


Figure 44. Reynolds Number of NSSC White Water

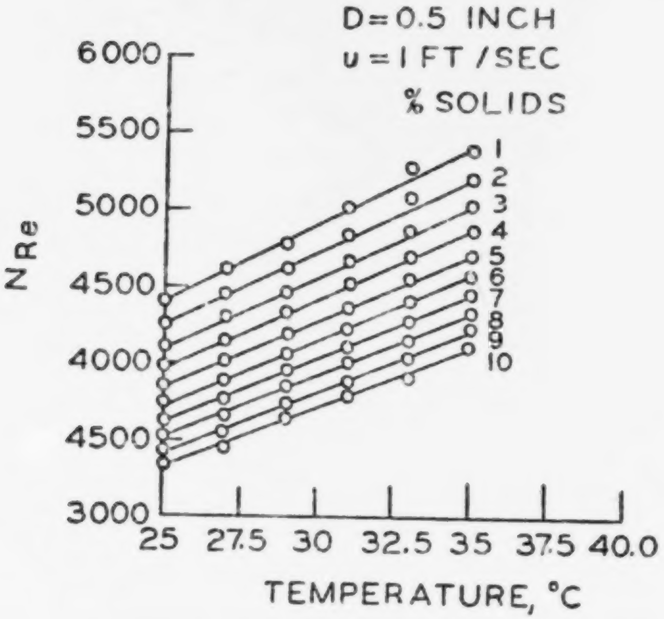


Figure 45. Reynolds Number of Ammonia-Base Acid Sulfite Liquor

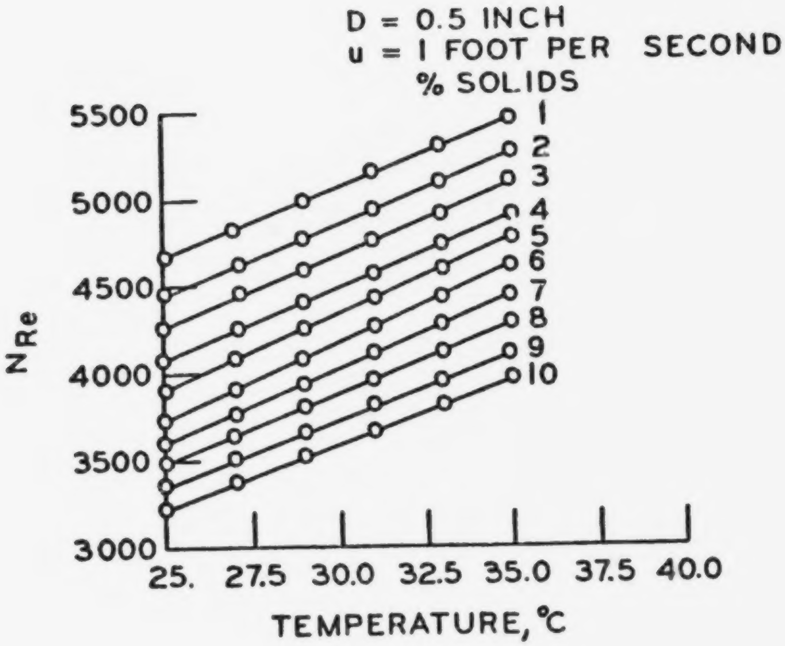


Figure 46. Reynolds Numbers of Calcium-Base Acid Sulfite Liquor

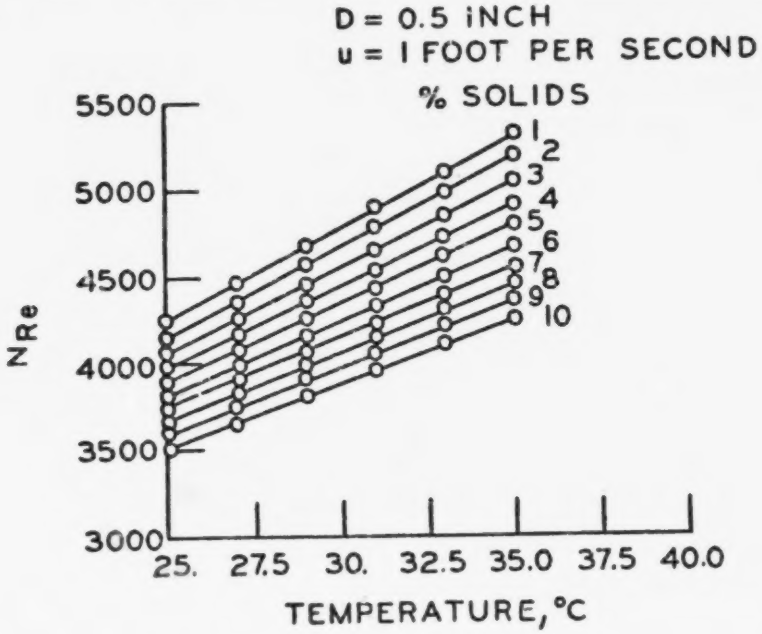


Figure 47. Reynolds Numbers of Kraft Bleach Effluent Liquor

second should be sufficient to produce turbulence at all temperatures indicated for a solids concentration of:

2.0 percent or less of NSSC white water.

3.0 percent or less of ammonia-base acid sulfite and second-stage kraft bleach effluent liquors

4.0 percent or less of calcium-base acid sulfite liquor flowing in a tube of 0.5 inch inside diameter.

For higher concentrations, a velocity of 1.0 ft/sec may or may not be turbulent, depending on the temperatures of the liquor. The optimum and maximum desirable velocities are, of course, at much higher levels, which are discussed in the following paragraphs.

Pressure Drop and Pumping Energy Requirements for a Commercially Available Tubular-Type Module

A next step in developing engineering design data for RO concentration processing of the four types of pulping and bleaching liquors involved determination of the pressure drop in a representative tubular module (Havens Model J 18-tube module having about 144 linear feet of 1/2-inch ID tubes in series). It was then possible to calculate the pumping energy as Kwh/1000 gallons which would be required to overcome this pressure drop. This is one of the important design factors of concern in the selection of the number of modules to be used in series. If the velocity is to be held constant, then by connecting a large number of modules in series, we limit the total flow rate going into the system; but at the same time, the pressure drop increases in proportion to the number of modules. Under such conditions, it becomes necessary to add booster pumps to overcome the pressure drop. Therefore, one has to optimize pressure drop against the total flow rate, while selecting the number of modules to be connected in series.

Pressure drops in the 18-tube modules used in this study were determined at different flow rates for 4 liquors and water.

Reynolds number, at different flow rates, were determined using the densities and viscosities of each liquor and water. Then the data for the pressure drops and N_{Re} were fitted to a log-log expression, using the method of least squares. Finally, the pressure drops at various values of N_{Re} were calculated from this expression, and the results are given in Fig. 48 at 35°C for about 10.0 percent solids concentrations of 4 liquors and water. The pH of each liquor was adjusted to 4.5.

Pressure drop at N_{Re} of 40,000 is highest (= 166 psig) for NSSC white water, and lowest (= 94 psig) for kraft bleach effluent liquor. This is true because viscosities of various concentrations of kraft bleach

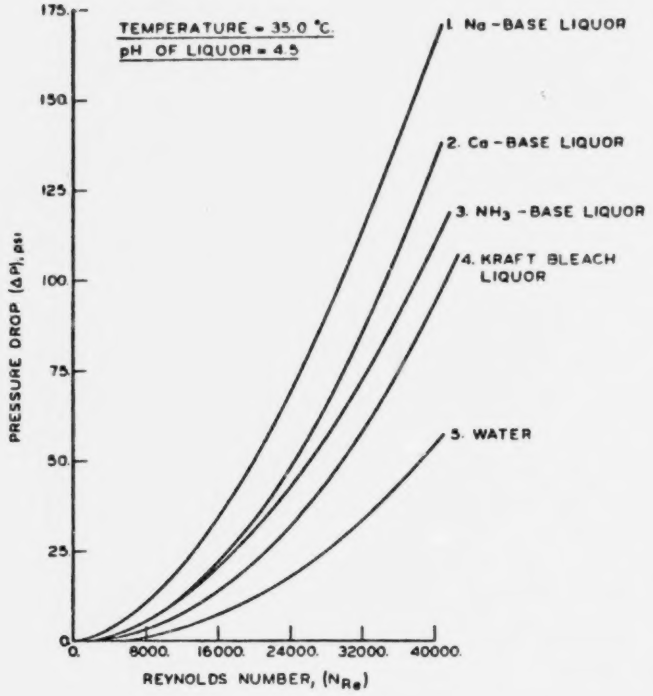


Figure 48. Frictional Pressure Drop in One 18 Tube Havens Module for 10 Percent Solids Liquors

effluent liquor were found to be lower than corresponding viscosities for NSSC white water at various concentrations.

From Fig. 48, the pressure drop may be observed to increase rapidly with increase in N_{Re}. This is true because the pressure drop is directly proportional to $(R_{Pe})^n$, where n varies from 1.75 to 2.00. The pressure drop in three identical 18-tube Havens modules connected in series was found equal to 3 times the pressure drop in a single 18-tube module. The higher the pressure drop, the lower the driving force, and the lower the flux rate. For example, in the case of three 18-tube modules connected in series, the pressure drop at N_{Re} = 40,000 for 103 g/l concentration of NSSC white water was 498 psig. So the average pressure of 351 psig for an inlet pressure of 600 psig can result in about 55 percent lower flux rates than the flux rates at 600 psig, even at 1.0 percent solids concentration of NSSC white water. Therefore, the pressure drop is a very important design factor in the selection of the number of modules to be connected in series.

Figure 49 gives the calculated pumping energy as Kwh per 1000 gallons of liquor to overcome the frictional pressure drop at various values of N_{Re}. The pumping energy curves follow a pattern similar to the

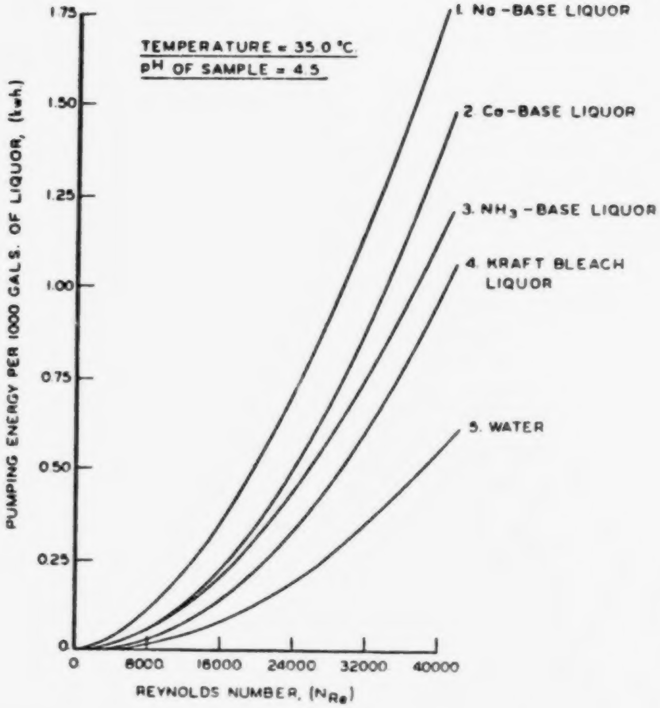


Figure 49. Pumping Energy in One 18-Tube Havens Module for 10.0 Percent Solids Liquor

pressure drop curves. The higher the pressure drop, the higher the pumping energy. The highest value of pumping energy, which is for NSSC white water, at 103 g/l concentration, was calculated to be 1.72 Kwh, compared to 0.56 Kwh for water under the same values of N_{Re} = 40,000. Therefore, the Kwh of pumping energy required for NSSC white water is 3 times that of water. The pumping energy is one of the important cost considerations in design and use of the RO process.

Determination of Osmotic Pressures

A next step in developing design data for effective RO processing of these 4 liquors was directed to determination of the effective driving force required for different concentrations of each liquor. The flux rate at any concentration of the liquor is directly related to the osmotic pressure of the liquor by the following equation:

$$F = A(\Delta P - \Delta\pi) \qquad (10)$$

where

F = flux rate through the membrane, gfd
A = membrane constant, gfd/psia

ΔP = difference between the applied pressure and the delivery pressure of product water, psia

$\Delta\pi$ = (difference between the osmotic pressures of the liquor and the product water) + (osmotic pressure increase due to concentration polarization and fouling effects, psia)

The product water is delivered at atmospheric pressure. Since the osmotic pressure of the product water is usually very small compared to the osmotic pressure of the liquor, the former term can be ignored. In the case of zero concentration polarization and fouling effects, the driving force ($\Delta P - \Delta\pi$) becomes equal to the difference between the applied pressure (P_A) and osmotic pressure of the liquor (π). Therefore, equation 10 becomes:

$$F = A(P_A - \pi) \tag{11}$$

From equation 11, it is apparent that the higher the osmotic pressure of the liquor, the lower the flux rate for a fixed applied pressure. In case of liquors having osmotic pressures higher than the applied pressure, there is osmotic flow across the membrane.

A vapor pressure Osmometer (VPO), which operates on the principle of vapor pressure lowering, was used to measure the osmotic pressures of each sample of liquor. An NaCl solution was used as a reference for the VPO. However, the VPO was useful only for determining the osmotic pressures of second-stage kraft bleach effluent liquor, and of the NSSC white water.

The osmotic pressures of calcium- and ammonia-base acid sulfite liquors could not be obtained by VPO, probably because of association and dis-association properties of lignosulfonates in these spent sulfite liquors, and were determined instead by measuring the flux rates at the different concentrations of each liquor.

These liquor flux rates were then compared with the flux rates of sodium chloride solutions of known osmotic pressure. All the flux rate runs were made at a higher velocity to minimize any increase in osmotic pressure due to concentration polarization and fouling. By solving equation 11 and the sodium chloride flux rate equation, $Fs = A(P_A - \pi_s)$, the following relationship is obtained for the osmotic pressure of the liquor:

$$\pi = P_A \left(1 - \frac{\pi_s}{P_A}\right) \left(1 - \frac{F}{Fs}\right) \tag{12}$$

where

π = osmotic pressure of the liquor, psia
P_A = applied pressure, psia

F = liquor flux rate, gfd
Fs = sodium chloride solution flux rate, gfd
π_s = difference between the osmotic pressures of sodium chloride solution and the product water, psia

By substituting the flux rates of sodium chloride and liquor at 600 psig, and the osmotic pressures of sodium chloride in equation 12, the osmotic pressures of calcium- and ammonium-base acid sulfite liquors were determined. The results are given in Fig. 50 at 25°C and at different concentrations of the 4 liquors.

From Fig. 50, it is apparent that the osmotic pressures for second-stage kraft bleach effluent liquor are very high compared to other liquors, and it increases linearly from 84.0 psia at 10.0 g/l to 594.0 psia at 100.0 g/l. This is understandable, because there is more inorganic material, especially NaCl, present in second-stage kraft bleach effluent liquor as compared to the other 3 liquors. The osmotic pressures of calcium-base acid sulfite liquor and NSSC white water increase linearly with the concentration, and are less than 300 psia for liquor solids concentrations up to 100 g/l. Ammonia-base acid sulfite liquor was found to have osmotic pressures greater than for calcium-base acid sulfite liquor and NSSC white water. In addition, the osmotic pressures of ammonia-base acid sulfite liquor do not vary linearly with the concentration.

Rejection Ratio

Dilute samples of each of the 4 liquors were concentrated from 1.0 to 10.0 percent solids by reverse osmosis. During these concentration runs, feed, concentrate, and product samples were taken. These samples were analyzed for solids, optical density (OD), biological oxygen demand (BOD_5), and chemical oxygen demand (COD). Rejection ratios (R) were calculated using the following formula:

$$R = (1 - Cp/Cc)100 \qquad (13)$$

where

Cp = concentration of product
Cc = concentration of feed to the module

The results are given in Table 76 at different concentrations of each liquor. Rejection of color based on OD measurements at 281 nm is good and ranged above 98.0 percent except in ammonia-base acid sulfite liquors. Ammonia-base sulfite liquors contain relatively low molecular weight colored materials, which are not completely rejected by Type 3 Havens cellulose acetate membrane. The rejection of solids is above 95.0 percent and range upward of that value in those liquors having good color rejections. BOD_5 rejections vary between 85.0-95.0 percent, and were observed to be significantly higher at upper levels of solids concentration for all types of spent liquors in these studies. COD

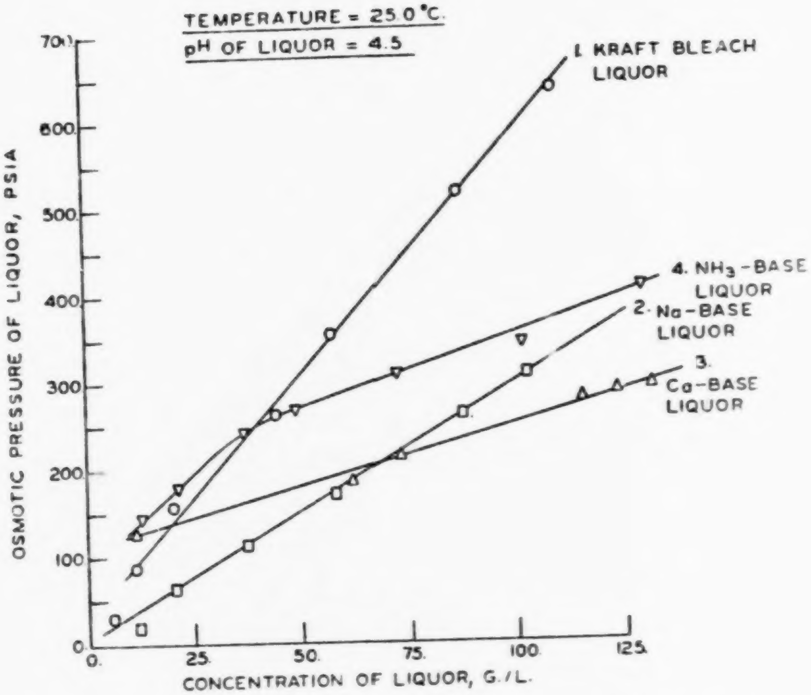


Figure 50. Osmotic Pressure vs. Concentration of the Liquor

rejections were found to be better than BOD_5 rejections and solids rejections, and were above 97.0 percent in most of the observations. The apparent anomaly with BOD_5 rejections being high at advanced stages of concentration, in some cases could be explained by permeation of low molecular weight organics, such as acetic acid, which are high in BOD_5 in early stages of concentration.

Product Flux Rate — Temperature Relationship

The effect of temperature on product flux rate was studied at 12.0 and 104 g/l solids concentration of calcium-base acid sulfite liquor. Figure 51 shows the percentage change is flux rate vs temperature between 20.0 and 43.0°C. For calcium-base acid sulfite liquor of concentration 12.0 g/l, there was 2.1 percent increase in flux rate for every rise in degree centigrade of temperature. The percentage increase in flux rate did not change significantly at 104.0 g/l concentration of the liquor. Flux rate variation with temperature is higher for water and is about 2.8 percent rise per °C rise[1]. According to Kopecek and Sourirajan[7], water flux rate increases due to increase in the membrane constant, which is related by the following expression at a given pressure.

$$A/\mu w = \text{constant} \qquad (14)$$

TABLE 76

REJECTION RATIOS (PERCENT) FOR 4 LIQUORS AT A CONCENTRATION OF 0.2 - 10 PERCENT SOLIDS

Inlet Pressure = 550-600 psig
pH of Liquor = 4.5 (Adjusted with H_2SO_4 or NaOH)
Inlet Velocity = 4-5 ft/sec
Type 3 Havens Modules

Sample	24-Hour Neut. Solids, g/l	Optical Density at 281 nm	BOD_5, mg/l	COD, mg/l	24-Hour Neut. Solids, g/l	Optical Density at 281 nm	BOD_5, mg/l	COD, mg/l
	Calcium-base acid sulfite liquor				NSSC white water			
1. Feed sample	11.4	82	2820	13910	11.0	58	1870	6220
2. Concentrate Samples No. 1.	39.5	267	10740	48120	1. 57.1	298	9475	58200
2.	91.6	675	24350	113680	2. 101.7	585	15900	127000
3. Permeate Samples No. 1.	1.23	3.9	864	1515	1. 1.47	1.3	854	1298
2.	2.93	8.8	2078	3356	2. 1.95	1.8	822	1670
4. Rejection ratios (percent) No. 1.	96.90	98.5	91.96	96.85	1. 97.42	99.55	90.90	97.77
2.	96.81	98.70	91.46	97.05	2. 98.08	99.70	94.84	98.69
	Ammonia-base acid sulfite liquor				Second stage kraft bleach effluent liquor			
1. Feed sample	10.8	102	3210	13620	2.8	16	189	1375
2. Concentrate Samples No. 1.	38.9	323	9650	49280	1. 19.4	117	955	11120
2.	115.9	995	28050	143800	2. 86.1	642	4295	47840
3. Permeate Samples No. 1.	0.96	12.5	809	1420	1. 0.84	0.5	103	186
2.	2.80	28.5	1910	3812	2. 5.13	1.1	256	413
4. Rejection ratios (percent) No. 1.	97.54	96.13	91.62	97.12	1. 95.65	99.60	89.21	98.33
2.	97.59	97.14	93.19	97.35	2. 94.04	99.83	94.05	99.14

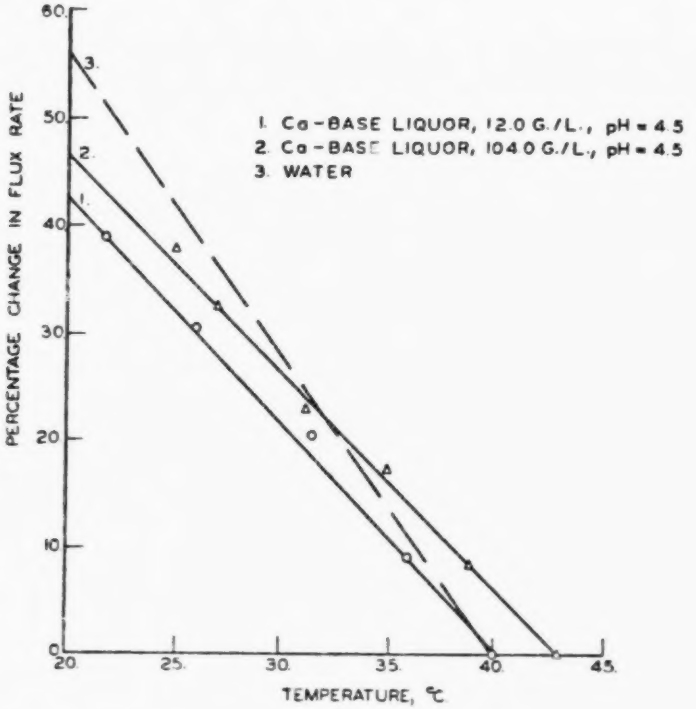


Figure 51. Effect of Temperature on Flux Rates of Water and Calcium-Base Acid Sulfite Liquor

where

A = pure water permeability constant, g-mole water/sq cm sec atm
μw = viscosity of water, centipoise

According to equation 14, the increase in flux rate with increase in temperature is a function of the decrease in viscosity of the solution. The larger the percentage change in viscosity of the liquor, the higher the percentage rise in flux rate. However, it is observed experimentally from Reynolds Number studies that the average decreases of viscosity per °C rise are 3.0 and 2.1 percent at 1.0 and 10 percent solids concentration of the liquor, respectively. This flux rate increase did not occur at the expense of hydrolysis of the cellulose acetate membrane. Hydrolysis of a membrane is a long-term effect, whereas flux rate-temperature effect is instantaneous. Of course, the rate of hydrolysis has been found to vary as the reciprocal of the absolute temperature[25] and it can result in increase in flux rate at the expense of percentage rejection.

Figure 51 shows that calcium-base acid sulfite liquor flux rate at 40.0°C will be 25.0 percent higher than the flux rate at 28.0°C.

Therefore, the higher the temperature, the higher the flux rate. We may conclude that temperature is an important parameter in the design of a reverse osmosis plant.

Effect of Velocity on the Flux Rates of NSSC White Water and Calcium-Base Acid Sulfite Liquor

Permeation Resistance *vs* Reynolds Number — NSSC White Water

The effect of velocity on flux rate is expressed in terms of permeation resistance, which in turn is determined by calculating the membrane constant. The membrane constant was determined by using the osmotic pressure and flux rate data of a known solution of sodium chloride. The permeation resistance (P_R) is calculated using the following equation as derived and discussed in the section on osmotic pressure determination:

$$P_R = P_A \left(1 - \frac{F_L}{F_s}\right) \left(1 - \frac{\pi_s}{P_A}\right) \qquad (15)$$

The above equation, P_R, is the sum of the osmotic pressure of the liquor and the osmotic pressure increase due to concentration polarization and fouling effects. The effect of velocity on flux rate is expressed in terms of permeation resistance because the permeation resistance becomes almost independent of applied pressure and velocity when running sodium chloride and liquor flux rates under identical conditions of velocity, pressure, and temperature.

A schematic diagram of the experimental setup is shown in Fig. 52. The feed was pumped at about 20 psig from a 500-gallon plastic tank to a main piston pump by a centrifugal feed pump. The main pump is a triplex reciprocating, positive displacement Manton Gaulin pump with a direct current motor and an electronic variable speed drive. For this study, the main pump discharged through 11 Havens modules (modified to contain only two tubes) at a pressure of 500 psig and flow rate varying from 1.2-4.3 gpm in each module. A pressure gage was installed at the inlet of each module. The flow rate of permeate was measured from each module. The total permeate of 11 modules was collected and mixed in a small tank and then drained to a 50-gallon plastic tank underneath the trailer. The permeate from a 50-gallon plastic tank was mixed with the concentrate via a small centrifugal Eastern pump. The recombined concentrate and permeate is returned through a heat exchanger for cooling and then recycles to the 500-gallon feed tank.

Three different concentration runs of NSSC white water were made at velocities of 2.0-7.0 feet per second. The sodium chloride solution flux rates were measured at 5.0 feet per second for each of the 11 two-tube modules before each concentration run. Each flux rate run was made at 500 psig and 35°C. The results of the permeation resistance calculated by using equation 12 are shown in Fig. 53. Because of the uncertainty as to accuracy of the osmotic pressures determined for

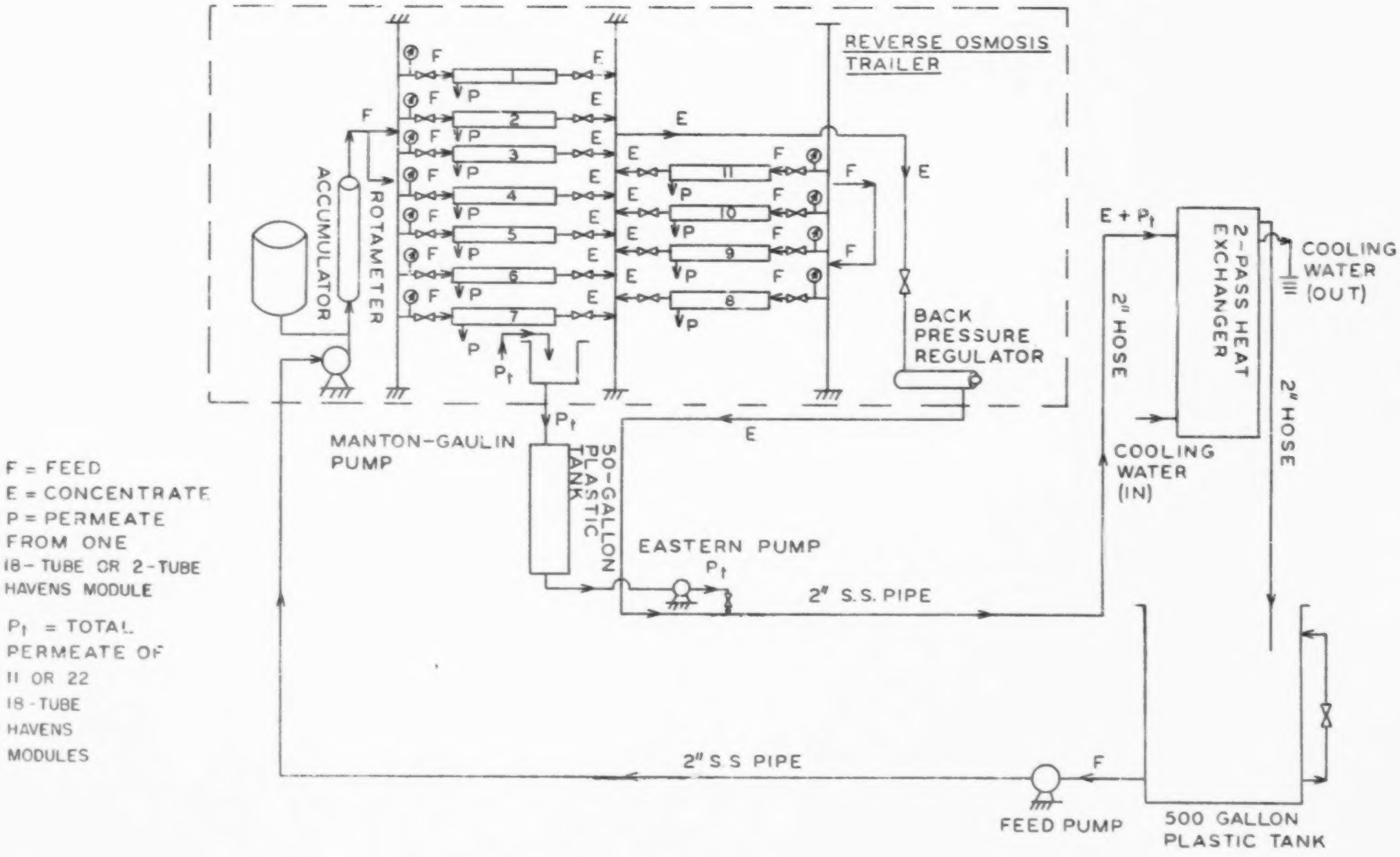

REVERSE OSMOSIS TRAILER
ACCUMULATOR
ROTAMETER
MANTON-GAULIN PUMP
50-GALLON PLASTIC TANK
EASTERN PUMP
2" S.S. PIPE
BACK PRESSURE REGULATOR
E + P_t
2" HOSE
2-PASS HEAT EXCHANGER
COOLING WATER (OUT)
COOLING WATER (IN)
2" HOSE
2" S.S PIPE
FEED PUMP
500 GALLON PLASTIC TANK
F
E
P
P_t
1
2
3
4
5
6
7
8
9
10
11
F = FEED
E = CONCENTRATE
P = PERMEATE FROM ONE 18-TUBE OR 2-TUBE HAVENS MODULE
P_t = TOTAL PERMEATE OF 11 OR 22 18-TUBE HAVENS MODULES

Figure 52. Schematic Diagram of Experimental Set-Up

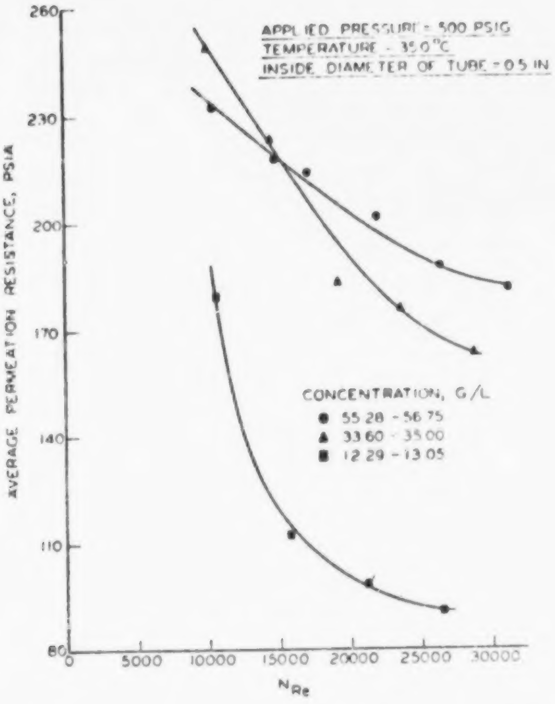


Figure 53. Permeation Resistance vs Reynolds Number — NSSC White Water

sodium chloride as used in equation 15, there is a uniform error in the permeation resistances and so the absolute values of the permeation resistances at the highest velocities of each concentration is different from the osmotic pressures of NSSC white water as shown in Fig. 50. Of course, the relative variations of the permeation resistances with velocities are quite accurate.

The permeation resistance was determined by measuring the flux rates of each module and then the average permeation resistance was calculated. In Fig. 53, three sets of curves represent permeation resistances at various values of N_{Re} for three different concentrations of NSSC white water. At the same concentration, the permeation resistance increased with decrease in N_{Re} due to increase in concentration polarization. At lower velocities, the increase in permeation resistance was quite significant. At lower concentrations of NSSC white water, the permeation resistance was lower because the osmotic pressure of the solution was substantially less for that type of feed liquor high in content of dissolved salts.

Velocities below which relatively higher permeation resistances were obtained, were estimated from the data shown in Fig. 53 and are given in Table 77. It is seen from Table 77 that the higher the concentration, the higher the velocity below which higher permeation resistance was observed. This is true because there is an increase in concentration polarization and fouling with increase in concentration.

TABLE 77

REYNOLDS NUMBER AND VELOCITIES OF NSSC WHITE WATER BELOW WHICH RELATIVELY HIGHER PERMEATION RESISTANCES ARE OBTAINED

Concentration, g/l	N_{Re}	Velocity in 1/2-Inch Tube, ft/sec
12.7	16000	3.00
34.3	19000	4.00
56.0	22000	5.00

Concentration Polarization and Fouling Study as a Function of Velocity for Calcium-Base Acid Sulfite Liquor

The effect of velocity on flux rate is expressed in terms of percentage decreases in flux rate from the starting flux rates. Here the same schematic diagram of the experimental setup as shown in Fig. 52 was used. A number of continuous flux rate runs were made at different concentrations of the liquor under controlled conditions of 35°C and 500 psig pressure. Before the start of each run, the modules were washed with high velocity water and with detergent BIZ solution of 15 g/l concentration. The percentage decrease in flux rate observed was less than 2.0 percent over a continuous run of 97 hours at 3.0 ft/sec and for 118 g/l concentration of the liquor. As it became very difficult to obtain fouling in case of a two-module setup, we decided to put nine 18-tube Havens modules in 3 manifolds, each manifold containing 3 modules in series. The remaining 8 manifolds had 2-tube modules. The flux rate of each of the nine 18-tube Havens modules were measured at different operating hours of the continuous run. The percentage decrease in flux rate from starting flux rate was determined and then the average percentage decrease in flux rate was calculated.

Figure 54 gives the average percentage decrease in flux rate vs hours of operation at two velocities of the liquor for concentrations above 10.0 percent solids of nonprecipitated calcium-base acid sulfite liquor. From Fig. 54, it is noted that the average percentage decrease in flux rate at 70 hours of operation is reduced from 8.0 to 4.0 percent by increasing the velocity from 0.8 to 1.2 ft/sec.

Figure 55 shows the effect of velocity on flux rate for calcium-base acid sulfite liquor in which there was a significant amount of precipitated calcium sulfate solids. The average percentage decrease in flux in this precipitated liquor is a strong function of velocity and it

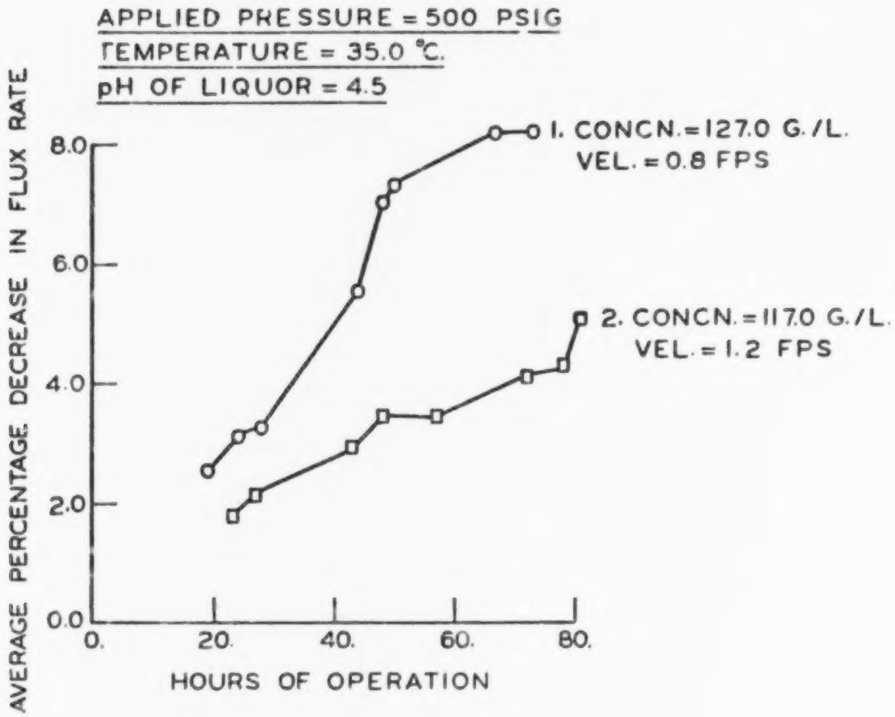


Figure 54. Effect of Velocity on the Flux Rates of Ca-Base Liquors (No Precipitate)

becomes less than 12.0 percent at 1.8 ft/sec over 50 hours of continuous operation. The conclusion is that velocity is an important parameter in controlling the decrease in flux rate which may result from scaling and fouling of membrane tubes.

Finally, it is noted that we have been able to control concentration polarization at velocities even below 1.5 ft/sec. Fouling has not been apparent in 70-hour runs at these low velocities. However, it is not economical to have such low velocities because the absolute value of flux rate increases with increase in velocity at a rate proportional to $V^{0.8}$[24]. At higher velocities, it becomes necessary to optimize this increase in flux rate against the loss of flux rate due to frictional pressure drop and the cost of pumping energy.

Microbiological Fouling

Fouling of the membrane surfaces by microbiological growth is often observed in sustained operations with wastes containing nutrients capable of promoting growth of bacterial yeast and molds. Where growth has developed significantly, flux rates may be restored by removing the growth with flows at high velocities, with the aid of detergents,

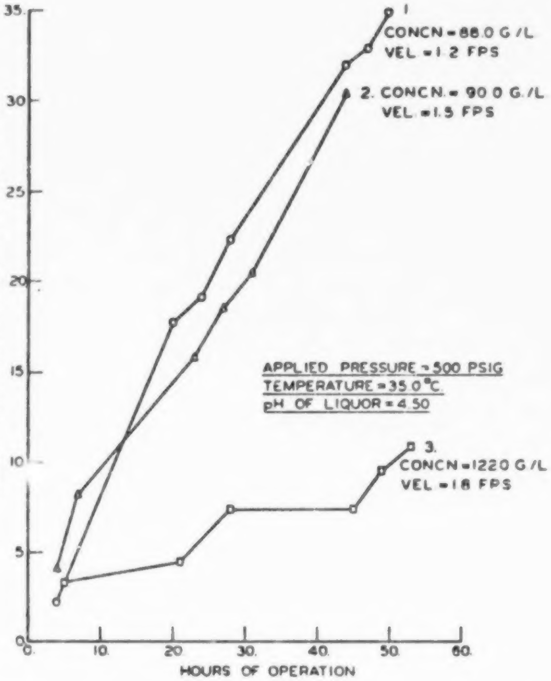


Figure 55. Effect of Velocity on the Flux
Rates of Ca-Base Liquor (Precipitate)

and by flushing plastic foam balls through the system periodically at intervals of several days to a week or more depending upon the degree of growth experienced. We have been concerned with finding ways to prevent or inhibit such growth, and high velocity appears to be an especially effective method of keeping the system clean or at least reducing the frequency of need for cleanups. Despite the extensive experience with microbiological fouling on sustained runs, we have been unable to observe and to maintain and to analyze fouling rates satisfactorily under carefully controlled conditions ranging to runs of as much as 120 hours of continuous operation with our standard test solutions made up of a calcium-base feed sulfite liquor. Significant increases in the resistance to permeation has been observed at lower velocity with neutral sulfite semichemical white water. These studies are being continued to more closely develop knowledge of the fouling rates and conditions for preventing the development of microbiological fouling.

Effect of Pressure on Membrane Compaction

Membrane compaction at elevated pressures should not be confused with microbiological fouling. At higher pressures, there is compaction of the porous membrane layer which results in a decrease in the membran constant and hence the flux rate. The flux rate decline due to reduced membrane constant does not seem to be at the expense of rejections. The rejection ratios for spent sulfite liquor do not show any significant increase with an increase in the membrane constant.

For this study, we set up 3 parallel rows of 3, Type 310 Ps-Series, Havens 18-tube modules in our large-scale reverse osmosis trailer unit. A number of continuous flux rate runs were made at different inlet pressures, 500-800 psig using 1.0 percent solids concentration of NSSC liquor. Each flux rate run was made for about 24 hours under controlled conditions of temperature, 35°C, and various inlet pressures. Before the start of each liquor run, the modules were washed with high velocity water and with detergent BIZ solution of 15 g/l concentration. Higher velocities, 4.2-4.6 feet per second, were maintained throughout all these runs to minimize any concentration polarization and fouling of the membrane. The flux rates of individual modules were measured at the end of each 24 hours continuous run. Then the membrane constant "A" was determined using the osmotic pressures of NSSC liquors.

Table 78 gives the effect of pressure on the membrane constant and rejection ratios for three Havens modules operating under identical conditions. Figure 56 plots the membrane constant _versus_ average operating pressure for these three modules. From Fig. 56, it is noted that the membrane constant decreases almost linearly with increase in pressure for all the three modules, and the rate of decrease in the membrane constant "A," as determined from the slope of the straight line, varies between 1.05×10^{-5} and 1.15×10^{-5}. The membrane constant and the flux rate decreases by about 17 percent due to membrane compaction with an increase in the operating pressure from 500 to 800 psig, whereas the rejection ratios do not show any significant change.

Finally, it is noted that the flux rate loss due to membrane compaction is very significant and one should include this effect while optimizing the increase in flux rate at higher pressure against the capital cost of modules, and the cost of pumping energy and membrane replacement.

CONCLUSIONS

A velocity of 1.0 ft/sec is sufficient to produce turbulent flow at temperatures to 35°C and at solids concentrations up to 4 percent for all four liquors. For high concentrations, a velocity of 1.0 ft/sec may or may not be turbulent depending on the temperatures of the liquor.

Pressure drop and pumping energy for the four pulping and bleaching effluents studies were maximum for NSSC white water and minimum for kraft bleach effluent liquors.

Kraft bleach effluent liquors had the highest osmotic pressures which increased linearly from 84.0 psia at 10.0 g/l solids to 594.0 psia at 100.0 g/l solids. The osmotic pressures of the other three liquors ranged to about 300 psia at 10.0 percent solids concentration.

TABLE 78

EFFECT OF PRESSURE ON THE MEMBRANE CONSTANT A AND REJECTION RATIOS

Feed Liquor Used = NSSC Liquor
Feed Liquor Temperature = 35°C
Average Flow Rate = 2.5 2.8 gpm = 4.2-4.6 ft/sec

Average Pressure, psig	Concentration of Liquor, g/1	Flux Rate, gfd			Percent Rejection Ratios of Comp. Permeate					Membrane Constant, $AX10^2$ gfd/psig		
		Module No. 1	Module No. 2	Module No. 3	Optical Density at 281 nm	Solids	COD	BOD_5	Sodium	Module No. 1	Module No. 2	Module No. 3
483	10.6	9.8	8.9	8.5	99.2	97.9	97.7	96.7	96.7	2.17	1.97	1.88
583	9.9	11.2	10.4	10.0	99.4	97.6	97.4	93.6	97.2	2.02	1.88	1.80
683	10.0	12.5	11.9	11.3	99.3	95.5	95.7	88.8	95.6	1.91	1.81	1.73
783	9.8	13.0	12.6	11.7	99.5	97.6	97.5	93.8	97.3	1.72	1.67	1.55

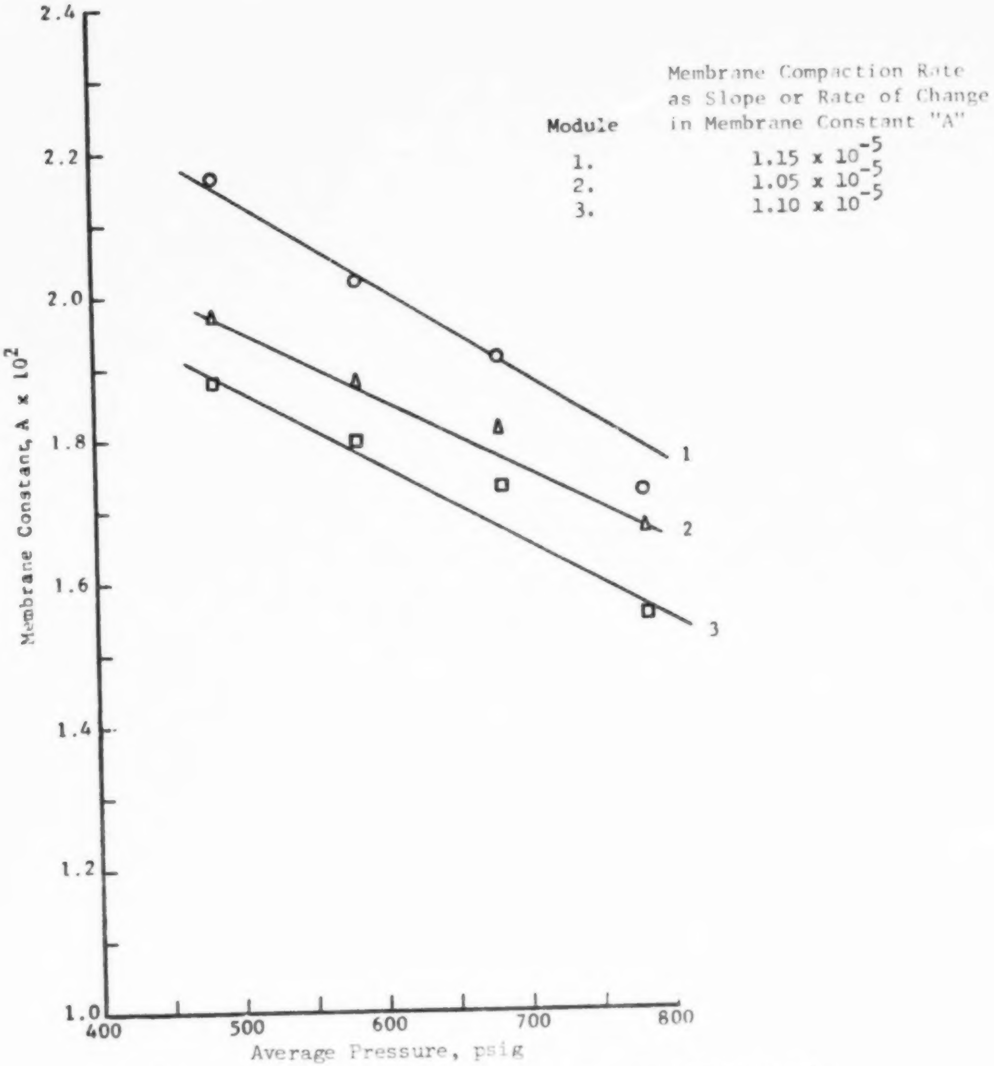


Figure 56. Membrane Constant vs Average Pressure (RO Studies)

Rejection of OD at 281 nm was above 98 percent for all liquors except for ammonia-base acid sulfite liquor, which averaged 97 percent. The rejection of solids was above 95.0 percent, whereas BOD$_5$ rejections varied between 85-95 percent. COD rejections ranged higher than for BOD$_5$ and for solids rejections.

The increase in flux rate per °C rise was 2.1 percent for calcium-base acid sulfite liquor in the solids concentration range of 1.0-10.0 percent. The flux rate increase with increase in temperature was higher for water, and was about 2.8 percent for each °C increase in temperature.

Reynolds Number of the order of 16000-22000 (equivalent to 3 to 5 ft/sec in a tube 0.5-inch inside diameter) may be necessary to prevent concentration polarization and fouling in 12-56 g/l concentrations range of NSSC white water. For 10 percent solids calcium-base acid sulfite liquor, the average decrease in flux rate over 70 hours of continuous operation was reduced from 8.0 to 4.0 percent by increasing the velocity from 0.8 to 1.2 ft/sec. This was true for liquors in which calcium salts had not precipitated. The flux rate decline observed in liquors in which precipitation of calcium salts occurred was observed to be relatively more dependent on the velocity.

The flux rate decreased by about 17 percent due to membrane compaction, with an increase in the operating pressures from 500 to 800 psig.

CONTROLLED STUDY OF MEMBRANE FOULING AND CONCENTRATION POLARIZATION

Membrane fouling problems have been a chief operating problem throughout the laboratory, pilot, and field demonstration studies conducted for this research and demonstration project. Such problems are well known to be of concern in other membrane research projects, such as in the saline water conversion field and various methods of reducing or eliminating the fouling effects have been developed. However, this project concerned with concentration processing of wood pulping and bleaching effluents has been especially involved with progressive loss in flux rates as the concentration process advances above 5 percent solids to desired levels of 10 percent solids for use as evaporator feeds. The problems have, therefore, been somewhat specialized and unique to this industrial waste treatment field. Progress has been made toward developing operating procedures to reduce the fouling effect but much has remained to be learned.

A series of carefully controlled studies of sufficient magnitude to provide a good statistical base (eleven sets of single modules in parallel and eleven sets of two in parallel) were conducted with close contro of velocity of flow, pressure, and temperature and of solids concentration. These studies permitted a much more careful analysis than had heretofore been possible for the effect of velocity of flow across the membrane surface in association with osmotic pressure effects occurring as the concentration increases. The study has gone far toward developing adequate answers to questions, and problems arising throughou the 4-year study, and have resulted in development of operating parameters to optimize the membrane concentration processing of the pulping and bleaching effluents.

The concentration polarization effects arising from low levels of velocity and turbulence can be associated with several other and apparently different sources or causes for fouling. A secondary "dynamically" formed membrane or film develops in the processing of some types of large molecular weight organics, such as the lignins contained in pulping liquors and has been much studied[23]. Plugging of the microporous structure of the basic cellulose acetate membrane by penetration of foulants is believed to be another separate and distinct cause of fouling. A sharp increase in osmotic pressure is especially apparent in concentrating substrate bleach liquors and pulping wash waters containing salts, such as NaCl and Na_2SO_4. Osmotic pressures in the upper levels of concentration of these substrates above 5 percent solids may reach 300 psig or even higher, and substantially reduce or even eliminate the effective driving force when operating pressures are in the 500 to 600 psig range, with resultant sharp fall-off in flux rates. Membrane compaction is another cause for reduction in flux rates which has been much studied. Evidence that membrane compaction can be a problem at elevated pressure above 700 psig has developed at times in this study, but this seems to be a matter of less concern than are fouling and concentration polarization at pressures below 700 psig.

In order to develop a better knowledge of the causative factors and to formulate operating parameters for optimum processing of these pulping and bleaching wastes, a series of systematic studies in moderately sized equipment were planned and initiated as reported on the following pages.

These studies were conducted in the Effluent Processes Group laboratories at The Institute of Paper Chemistry using Havens modules in the pilot-scale units and also in the large-scale trailer-mounted field demonstration unit which had been moved to the Institute campus. The feed liquors employed in these studies were prepared at various concentrations in 50 to 500 gallon batch quantities by diluting various evaporated concentrates, digester liquors and bleach effluent concentrates with tap water. The concentration of the feed was kept constant throughout each of these studies by recycling both the concentrate and permeate back to the feed tank.

This report describes two areas of study, first on the concentration and fouling relationships in Ca-base and NH_3-base pulp wash waters, and secondly on the permeation resistance vs velocity relationship for Ca-base acid sulfite, NSSC and for KBE effluents; concentration polarization and fouling as functions of velocity for Ca- and NH_3-base acid sulfite liquor.

The objective of this study was to determine the velocity required to overcome concentration polarization and fouling of tubular reverse osmosis systems. This is one of the chief factors of concern in maintaining high flux rates and of minimizing capital and operating costs.

For this study we used the large-scale trailer unit equipped with from 21 to 22 Type 310 R-Series Havens 18-tube modules. This number of modules was sufficient to achieve a statistical base for interpreting results. The feed liquor was maintained at about 10 percent solids and was prepared by diluting evaporated Ca-base SSL concentrate with tap water. The experimental setup for the trailer unit was the same as described previously for the velocity studies and as shown in Fig. 52.

A number of continuous flux rate runs were made at different velocities using 95-130 g/1 concentrations of Ca and NH_3-base liquors. Each flux rate run was conducted continuously for periods ranging from 70 to 100 hours under carefully controlled conditions of 35°C and 500 psig pressure. Before the start of each run, the modules were washed with high velocity water and with detergent BIZ solution of 15 g/1 concentration.

The flux rates of each of the modules were measured and expressed in terms of the percentages of the initial starting flux rate at different operating hours of the continuous run. Then average percentages of initial starting flux rates were determined at various hours of operation. The flux rate velocity studies were made for two different module configurations:

> Eleven 18-tube Havens modules — 11 parallel rows with one module in each parallel row.
>
> Twenty-two 18-tube Havens modules — 11 parallel rows of two modules in series in each parallel row.

Tables 79 and 80 give the effects of velocity on flux rate declines and rejection ratios due to concentration polarization and fouling of the membrane for Ca- and NH_3-base acid sulfite liquors. Figures 57 and 58 plot average percentage of initial flux rate versus hours of operation for a setup of 11 Havens modules at various velocities and at about 9-13 percent solids concentrations of the liquors. From Fig. 57 it can be noted that the average percentage of the initial flux rate at 72 hours of operation for Ca-base liquor increases from 88 to 92 percent by increasing the velocity from 2.4 to 4.5 feet per second. For NH_3-base liquor, Fig. 58 shows that the average percentage of the initial flux rate at 72 hours increases from 90 to 97 percent, with an increase in velocity from 1.8 to 4.5 feet per second. Tables 79 and 80 list the average percentages of the initial flux rate at 24, 48, and 72 hours, along with the average percentage rejection ratios of solids, optical density, COD, BOD_5, calcium and nitrogen for various velocities of Ca- and NH_3-base liquors. For 22 modules set up in 11 parallel rows of 2 modules in series, the average percentage of the initial flux rate at 72 hours and at 1.7-1.8 feet per second becomes 83 percent for Ca-base liquor and 89 percent for NH_3-base liquor. The rejection ratios of solids, OD, COD, calcium and nitrogen are all above 96 percent, whereas the BOD_5 rejections vary between 85 and 95 percent. The rejection ratios and the average percentage of the initial flux rate are higher at higher velocities, which indicates that there is decrease in concentration polarization and fouling of the membrane with increase in the velocity.

TABLE 79

EFFECT OF VELOCITY ON FLUX RATE DECLINES AND REJECTION RATIOS DUE TO CONCENTRATION POLARIZATION AND FOULING FACTORS FOR CALCIUM-BASE ACID SULFITE LIQUOR

Inlet Pressure = 500 psig
Concentration of Liquor = 120-127 g/l
Feed Liquor Temperature = 35°C
pH of Feed Liquor = 4.5

Average Velocity in 1/2" Tube, ft/sec	Average Flux Rate, gfd	Average Percent of Initial Flux Rate			Average Percent of Rejection Ratios				
		24 Hours	48 Hours	72 Hours	OD at 281 nm	Solids	COD	BOD_5	Calcium
Eleven 18-tube Havens modules — 11 parallel rows of one module in series in each parallel row									
2.4	5.0-6.6	92	90	88	99.6	98.6	97.4	92.7	99.6
3.5	5.5-7.7	97	94	--	99.7	98.9	96.2	92.0	99.7
4.5	5.0-7.1	98	96	92	99.3	98.6	98.2	95.4	99.5
Twenty-two 18-tube Havens modules — 11 parallel rows of 2 modules in series in each parallel row									
1.8	4.0-6.0	90	88	85	99.2	98.3	96.5	88.0	99.4
1.7	4.0-5.4	88	85	83	99.3	98.3	96.7	88.5	99.5

TABLE 80

EFFECT OF VELOCITY ON FLUX RATE DECLINES AND REJECTION RATIOS DUE TO CONCENTRATION POLARIZATION AND FOULING FACTORS FOR AMMONIA-BASE ACID SULFITE LIQUOR

Inlet Pressure = 500 psig
Concentration of Liquor = 95-106 g/l
Feed Liquor Temperature = 35°C
pH of Feed Liquor = 4.5

Average Velocity in 1/2" Tube, ft/sec	Average Flux Rate, gfd	Average Percent of Initial Flux Rate			Average Percent of Rejection Ratios				
		24 Hours	48 Hours	72 Hours	OD at 281 nm	Solids	COD	BOD_5	Nitrogen Ammonia
Eleven 18-tube Havens modules — 11 parallel rows of one module in series in each parallel row									
1.8	4.6-6.6	97	93	90	99.1	98.4	95.7	89.9	97.9
2.4	3.7-6.0	97	95	93	99.5	99.4	98.4	91.5	96.3
3.6	5.7-7.1	98	95	95	99.2	99.0	94.3	89.5	98.0
4.5	4.5-7.3	99	97	97	99.4	98.9	97.3	90.5	97.8
Twenty-two 18-tube Havens modules — 11 parallel rows of 2 modules in series in each parallel row									
1.8	5.0-6.7	96	92	90	99.9	98.3	97.7	85.5	95.8
1.7	4.5-6.5	95	90	89	99.9	98.3	97.7	86.0	96.4

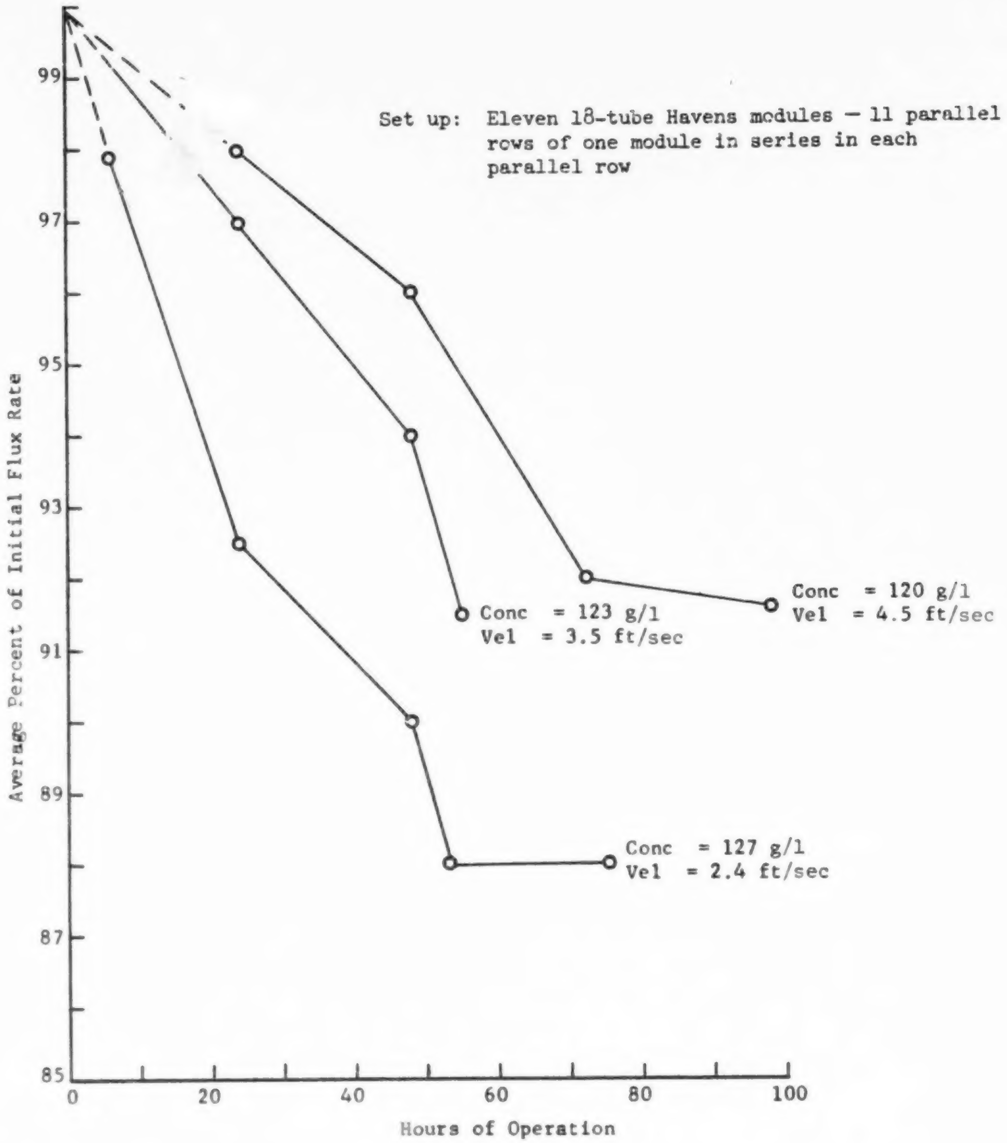


Figure 57. Effect of Velocity on Flux Rate Declines Due to Concentration Polarization and Fouling Factors for Calcium-Base Acid Sulfite Liquor (RO Studies)

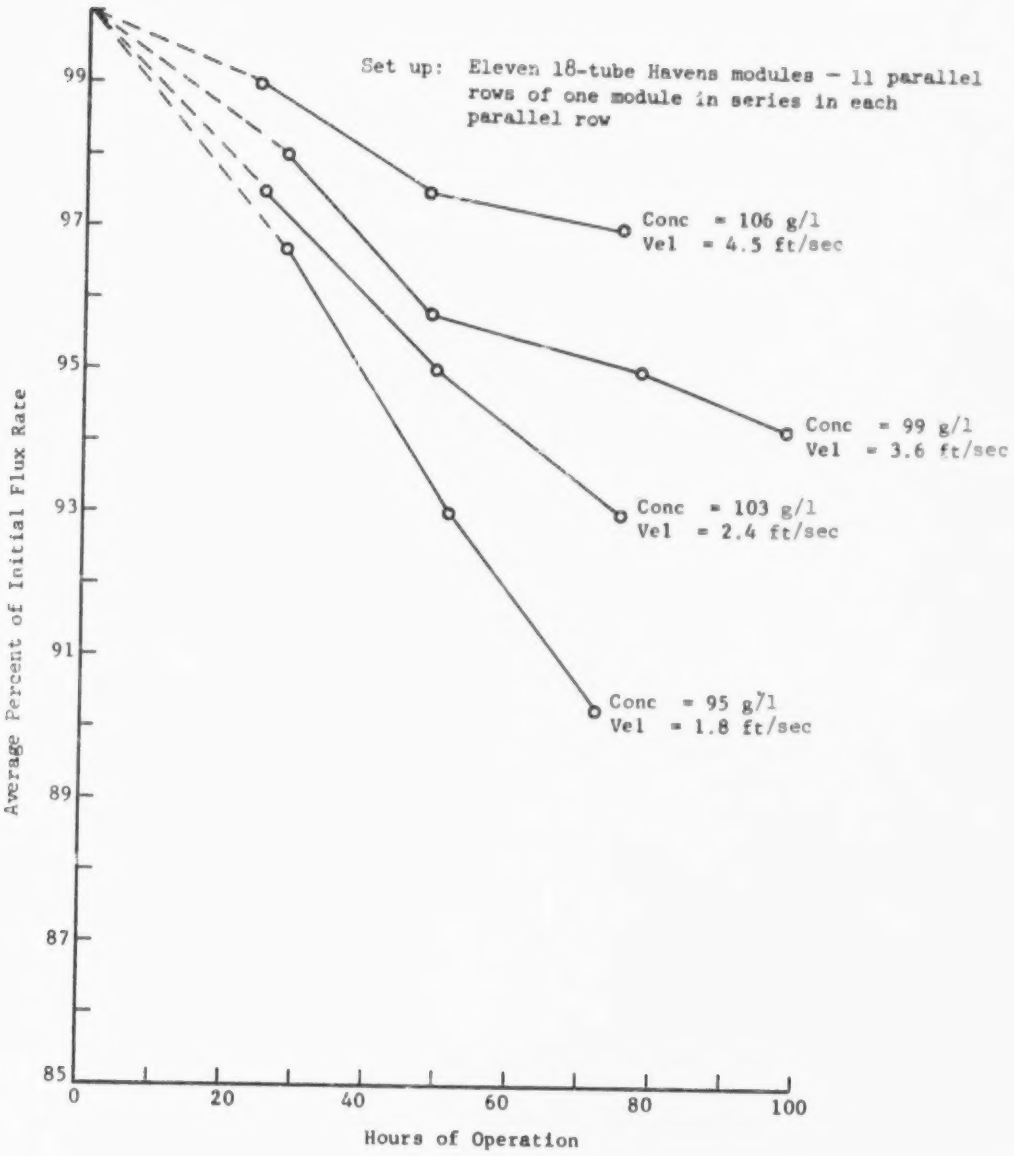


Figure 58. Effect of Velocity on Flux Rate Declines Due to Concentration Polarization and Fouling Factors for Ammonia-Base Acid Sulfite Liquor (RO Studies)

Finally, it is noted that we were apparently able to operate with freedom from concentration polarization and fouling at velocities even below 2.0 feet per second. We had little or no evidence of fouling of the membrane surfaces by microbiological growth in 70-100 hour runs at these low velocities. However, it would not be economical to employ such low velocities because the absolute value of flux rate increases significantly with increase in velocity. This effect of velocity on the absolute values of flux rates is discussed in the next section of this report.

Permeation Resistances — Velocity Relationship for Calcium-Base Acid Sulfite, NSSC, and Kraft Bleach Effluent Liquors

The objective of this study was to determine the effect of velocity on the absolute values for the flux rate. It has been observed by Aggarwal and Sourirajan[24] that the flux rate increases with increase in velocity at a rate proprotional to $V^{0.8}$. This is true because the thickness of the concentration boundary layer decreases, and so the mass transfer coefficient increases with increase in velocity. At higher velocities, it becomes necessary to optimize this increase in flux rate against the loss of flux rate due to frictional pressure drop and the cost of pumping energy. Therefore, this study is important in determination of the optimum velocity, not from the point of view of overcoming concentration polarization and fouling, but from the point of view of increasing the rate of mass transfer.

The effect of velocity on flux rate is expressed in terms of permeation resistance, which in turn is determined by calculating the membrane constant. The membrane constant was determined by running sodium chloride solution flux rates. The permeation resistance is calculated using equation (15).

We used our pilot-scale Milton Roy duplex test stand with pumping capacity up to 6 gallons per minute. The feed liquor was pumped from a 50-gallon plastic tank and its concentration was kept constant by recycling both the concentrate and permeate back to the feed tank.

In this study, we used a single Havens module modified to contain only two tubes at a pressure of 500 psig and velocity varying from 0.2 to 7.8 feet per second. A number of continuous flux rate runs were made for about 8 hours at different velocities and at about 1.0 and 10.0 percent solids concentrations of the liquors. The sodium chloride solution flux rates were measured at 4.0 feet per second before each new concentration run. All the flux rate runs were made under constant concentration conditions at 35°C and 500 psig pressure. Before the start of each liquor run, the module was washed with high velocity water and with detergent BIZ solution of 15 g/l concentration. The module was also subjected to a "hard pulsing" treatment during all the liquor runs to minimize the fouling effects.

Table 81 gives the effect of velocity on permeation resistances and rejection ratios for about 1.0 and 10.0 percent solids concentrations of Ca-base acid sulfite, NSSC and kraft bleach effluent liquors. Figure 59 plots permeation resistance versus velocity at various concentrations of the liquors. From Fig. 59, it is noted that the permeation resistances decrease considerably with increase in the velocity. The permeation resistances decrease by about 40-70 percent up to a velocity of 2 to 3 feet per second. The rejection ratios also increase with increase in the velocity of the liquor. Above a velocity of 3 feet per second, the permeation resistances do not show any significant decrease which probably indicates that the mass transfer rate becomes constant above this velocity.

Therefore, it may be necessary to maintain a minimum velocity of 3 feet per second (2 gallons per minute) for maximizing the mass transfer rate and hence the flux rate. But one must optimize this increase in flux rate against the loss of flux rate due to frictional pressure drop and the cost of pumping energy.

CONCLUSIONS

Minimum velocities as low as 2 feet per second may be required to overcome concentration polarization and fouling effects up to 10 percent solids concentration of Ca and NH_3-base acid sulfite liquors. However, it may not be economical to have such low velocities from the point of view of maximizing the mass transfer rates. It may at times be necessary to maintain a minimum velocity of 3 feet per second for maximizing the mass transfer rates and hence the flux rates.

DEVELOPMENT OF A COMPUTERIZED MATHEMATICAL MODEL FOR THE OPTIMAL DESIGN OF LARGE-SCALE REVERSE OSMOSIS SYSTEMS

A third area for supplementary engineering and development for this project has been directed to a systematic study of variables for the optimum design of large-scale reverse osmosis units to be used for concentrating dilute effluents of the pulp and paper industry. One of the first and important objectives was to determine the number of membrane modules and their best configuration for large, multiple-stage concentrating systems. This is one of the important factors in optimizing the capital and operating costs for the RO process.

For this study, a computerized mathematical model was formulated using design data developed with the pilot plant and large-scale trailer units. Parameters were established for verification of the mathematical model, and confirming trials were conducted for processing the various types of effluents on which demonstrations were conducted within this project. The formulations developed were then utilized in developing some of the economic data and conclusions reported in Section X.

TABLE 81

EFFECT OF VELOCITY ON THE PERMEATION RESISTANCES AND REJECTION RATIOS — CALCIUM-BASE ACID SULFITE LIQUOR, NSSC LIQUOR, AND KRAFT BLEACH EFFLUENT LIQUOR

Inlet Pressure = 500 psig
Feed Liquor Temperature = 35°C

Average Velocity in 1/2" Tube, ft/sec	Liquor Flux Rate, gfd	Permeation Resistance, psia	Percent Rejection Ratios				
			OD at 281 nm	Solids	COD	BOD$_5$	Calcium or Sodium
Calcium-base acid sulfite liquor — concentration = 13 g/l							
0.2	6.5	211	98.1	95.4	95.2	89.9	98.3
0.5	7.1	126	98.5	97.8	97.7	94.2	99.2
0.9	7.7	93	98.8	98.3	98.2	96.2	99.2
1.7	8.0	74	98.9	98.5	98.5	95.0	99.7
2.5	8.4	56	99.0	98.6	98.5	96.2	99.4
Calcium-base acid sulfite liquor — concentration = 128 g/l							
0.4	2.3	410	99.1	97.3	96.8	87.3	99.2
0.9	3.7	345	99.3	97.7	97.1	88.2	99.4
1.8	5.0	290	99.2	98.3	98.0	94.9	99.6
2.5	5.4	270	99.2	98.5	98.3	95.6	99.6
3.3	5.7	260	99.2	98.6	98.4	94.8	99.7
NSSC liquor — concentration = 10 g/l							
0.3	3.3	368	97.1	82.2	81.2	51.2	84.6
0.5	4.1	329	97.5	83.9	82.8	52.6	85.2
0.9	5.3	278	97.9	86.0	88.6	55.9	89.3
1.7	6.3	235	98.3	88.7	89.0	61.4	91.2
Kraft bleach effluent liquor — concentration = 10 g/l							
0.2	6.8	285	99.8	97.5	95.4	89.7	--
1.1	8.2	240	99.9	98.5	97.0	94.1	--
2.0	10.6	163	99.9	98.7	99.7	95.1	--
2.9	12.1	112	99.9	98.9	99.8	95.0	--
5.1	12.7	95	99.9	99.1	99.8	96.9	--
Kraft bleach effluent liquor — concentration = 115 g/l							
0.3	1.7	447	99.8	96.2	86.7	84.3	--
1.2	3.3	394	99.9	97.1	91.0	90.0	--
3.0	5.1	340	99.9	97.5	92.7	92.1	--
5.1	5.5	325	--	--	--	--	--
7.8	5.8	317	99.9	97.5	92.3	92.2	--

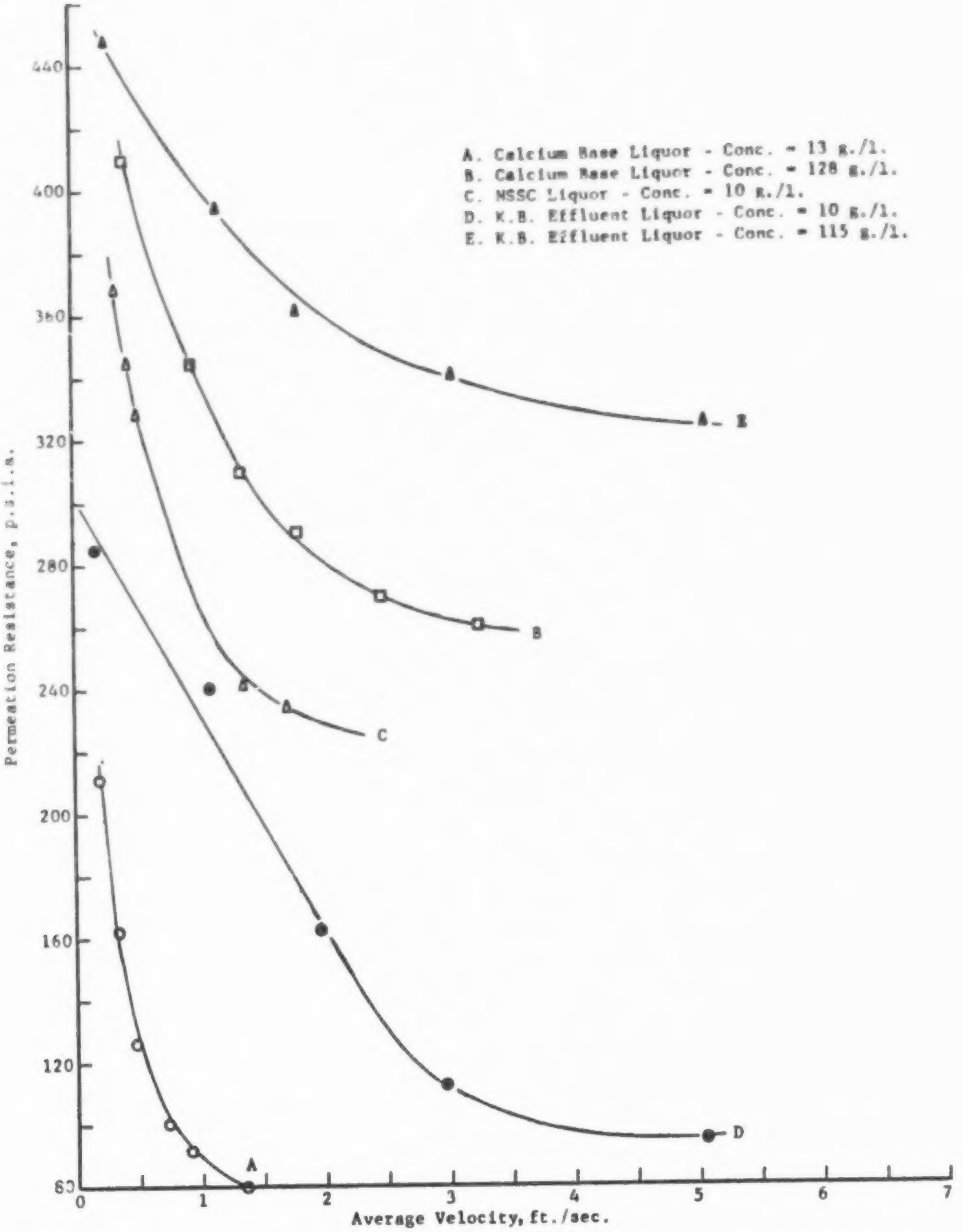


Figure 59. Velocity vs. Permeation Resistance — Calcium-Base Acid Sulfite, NSSC and Kraft Bleach Effluent Liquors (RO Studies)

DEVELOPMENT OF THE DATA AND THE MODEL

Basic Formulation and Computer Utilization in Setting Up a Mathematical Model

The basic formulations used in developing a mathematical model of an RO concentrating system are two simple equations of flux rate and rejection ratios. For a semipermeable membrane, the flux rate and rejection ratio are given by equations (10) and (13). Here the rejection ratio is defined as the ratio between the concentrations at both sides of the membrane at a certain spot and it is an important parameter in characterizing the quality of permeate for the processes of concentrating dilute feed or separating chemicals.

Manual computations of equations (10) and (13) for a multistage reverse osmosis system requires a substantial number of man hours. Also, the flexibility of the RO system is greatly limited by the speed of manual computation. In addition, many complexities are introduced in the solutions of the above equations by the following factors:

Effect of temperature and higher operating pressure on the membrane constant.

Variation of the osmotic pressures of the liquors with the concentration.

Need of higher velocities to overcome concentration polarization and fouling effects. Higher velocities cause large pressure drops, thus decreasing the driving force across the membrane.

In order to overcome this limitation, a computer program was written in Fortran IV language[2]. Such a program is designed to calculate the number of the following important factors for concentrating a certain volume of feed with a given feed concentration and a given percentage recovery ratio of water in more than one concentrating stage:

Number of modules and their arrangement in each concentrating stage.

Feed recycle ratio, inlet and outlet velocities, and percent recovery ratios of water in each stage.

Flux rate and concentration of the concentrate in each stage.

Capital and operating costs.

The program is very flexible and has been written in such a way that the effect of any of the variables can be studied without changing its internal format. The program takes less than 2 minutes for one complete calculation of the optimum number of modules, along with the capital and operating costs of an RO unit.

Flow Chart and Fortran Listing of a Computer Program

The flow chart of the computer program is given in Fig. 60 for better understanding of the sequence of operations involved in these optimization studies. In this flow chart, a trapezoid symbol[27] indicates an input or output operation, whereas a rectangular box indicates any processing operation except a decision. The "decision" is denoted by a diamond symbol. READ stands for the input data of the program, whereas WRITE gives the final output results of the program. The symbolic notation of various parameters of the input and output data and other important variables is also given along the flow chart.

There are three important decision checks made by the computer program. First, it checks the velocity at each stage of concentration and, if necessary, chooses a proper recycle ratio to maintain that velocity. Second, it checks the final effluent concentration of the last stage against the ultimate goal concentration and then changes the number of parallel rows in one or all the stages, depending upon the deviation between these two concentrations. Last, it compares each time new values of capital and operating costs with the previous corresponding costs, and then, if necessary, changes the number of modules in series in each parallel row until both capital and operating costs are minimum.

SYMBOLIC NOTATIONS OF VARIOUS INPUT DATA USED IN THE COMPUTER PROGRAM

DGD = Design capacity of RO unit, gal./day
CIN = Initial concentration of the feed, g/l
COUT = Final concentration of the concentrate, g/l
D = Tube inside diameter, inch
SA = Module surface area, sq ft
AP = Reference inlet pressure, psig
TEMP = Reference feed temperature, °C
FLNA = Reference NaCl solution (5000 ppm) flux rate at 600 psig and 35°C, gfd
PINA = Reference osmotic pressure of NaCl solution, psia
AFL = Approximate average liquor flux rate at "AP" pressure and "TEMP" temperature, gfd
VC1, VC2 = Velocity (ft/sec) — concentration (g/l) relationship
OPC1, OPC2 = Osmotic pressure (psia) — concentration (g/l) relationship
RRC1, RRC2 = Rejection ratios (percent) — concentration (g/l) relationship
PDC1, PDC2 = Frictional pressure drop (psi) — concentration (g/l) relationship
PDV1, PDV2 = Frictional pressure drop (psi) — velocity (ft/sec) relationship
CRCAM = Membrane compaction rate
PINF = Percent increase in flux rate per degree centigrade

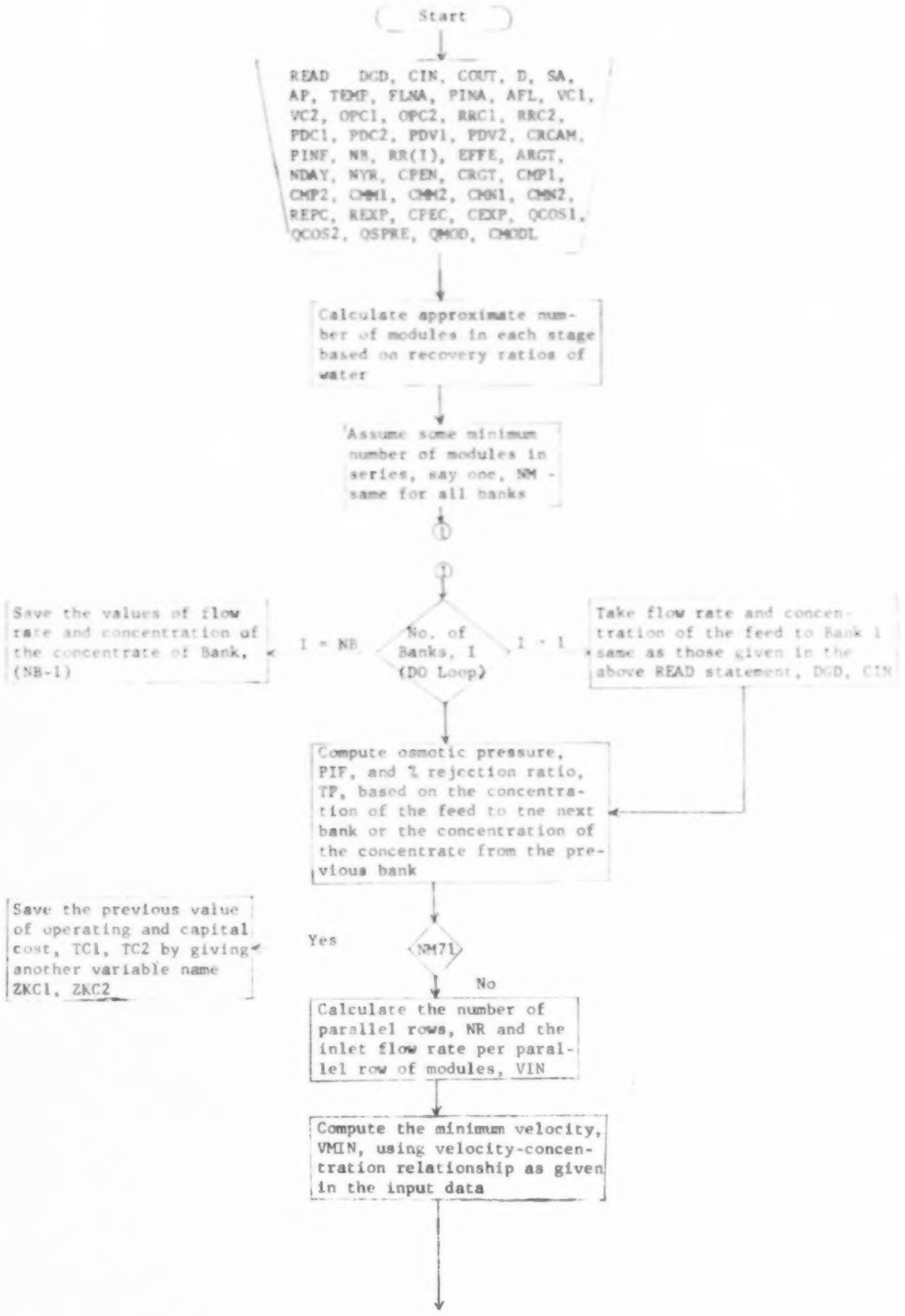

Start
READ DGD, CIN, COUT, D, SA, AP, TEMP, FLNA, PINA, AFL, VC1, VC2, OPC1, OPC2, RRC1, RRC2, PDC1, PDC2, PDV1, PDV2, CRCAM, PINF, NB, RR(I), EFFE, ARGT, NDAY, NYR, CPEN, CRGT, CMP1, CMP2, CMM1, CMM2, CMN1, CMN2, REPC, REXP, CPEC, CEXP, QCOS1, QCOS2, QSPRE, QMOD, CMODL
Calculate approximate number of modules in each stage based on recovery ratios of water
Assume some minimum number of modules in series, say one, NM - same for all banks
①
①
Save the values of flow rate and concentration of the concentrate of Bank, (NB-1)
I = NB
No. of Banks, I (DO Loop)
I = 1
Take flow rate and concentration of the feed to Bank 1 same as those given in the above READ statement, DGD, CIN
Compute osmotic pressure, PIF, and % rejection ratio, TP, based on the concentration of the feed to the next bank or the concentration of the concentrate from the previous bank
Save the previous value of operating and capital cost, TC1, TC2 by giving another variable name ZKC1, ZKC2
Yes
NM71
No
Calculate the number of parallel rows, NR and the inlet flow rate per parallel row of modules, VIN
Compute the minimum velocity, VMIN, using velocity-concentration relationship as given in the input data

Figure 60. Flow Chart of Reverse Osmosis Optimization Studies

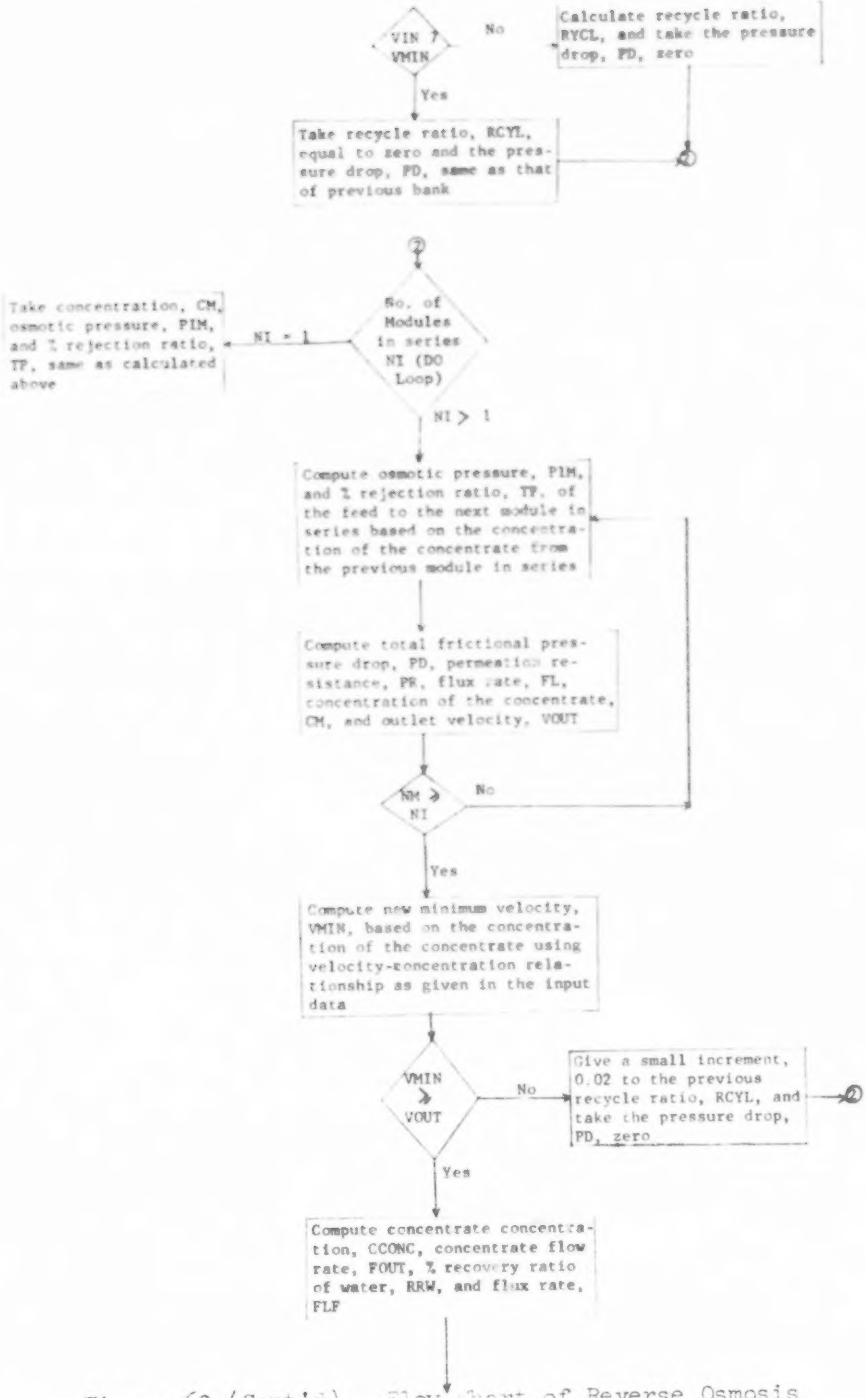

VIN ≥ VMIN
No
Calculate recycle ratio, RYCL, and take the pressure drop, PD, zero
Yes
Take recycle ratio, RCYL, equal to zero and the pressure drop, PD, same as that of previous bank
②
②
No. of Modules in series NI (DO Loop)
NI = 1
Take concentration, CM, osmotic pressure, PIM, and % rejection ratio, TP, same as calculated above
NI > 1
Compute osmotic pressure, PIM, and % rejection ratio, TP, of the feed to the next module in series based on the concentration of the concentrate from the previous module in series
Compute total frictional pressure drop, PD, permeation resistance, PR, flux rate, FL, concentration of the concentrate, CM, and outlet velocity, VOUT
NM ≥ NI
No
Yes
Compute new minimum velocity, VMIN, based on the concentration of the concentrate using velocity-concentration relationship as given in the input data
VMIN ≥ VOUT
No
Give a small increment, 0.02 to the previous recycle ratio, RCYL, and take the pressure drop, PD, zero
②
Yes
Compute concentrate concentration, CCONC, concentrate flow rate, FOUT, % recovery ratio of water, RRW, and flux rate, FLF

Figure 60 (Cont'd). Flow Chart of Reverse Osmosis Optimization Studies

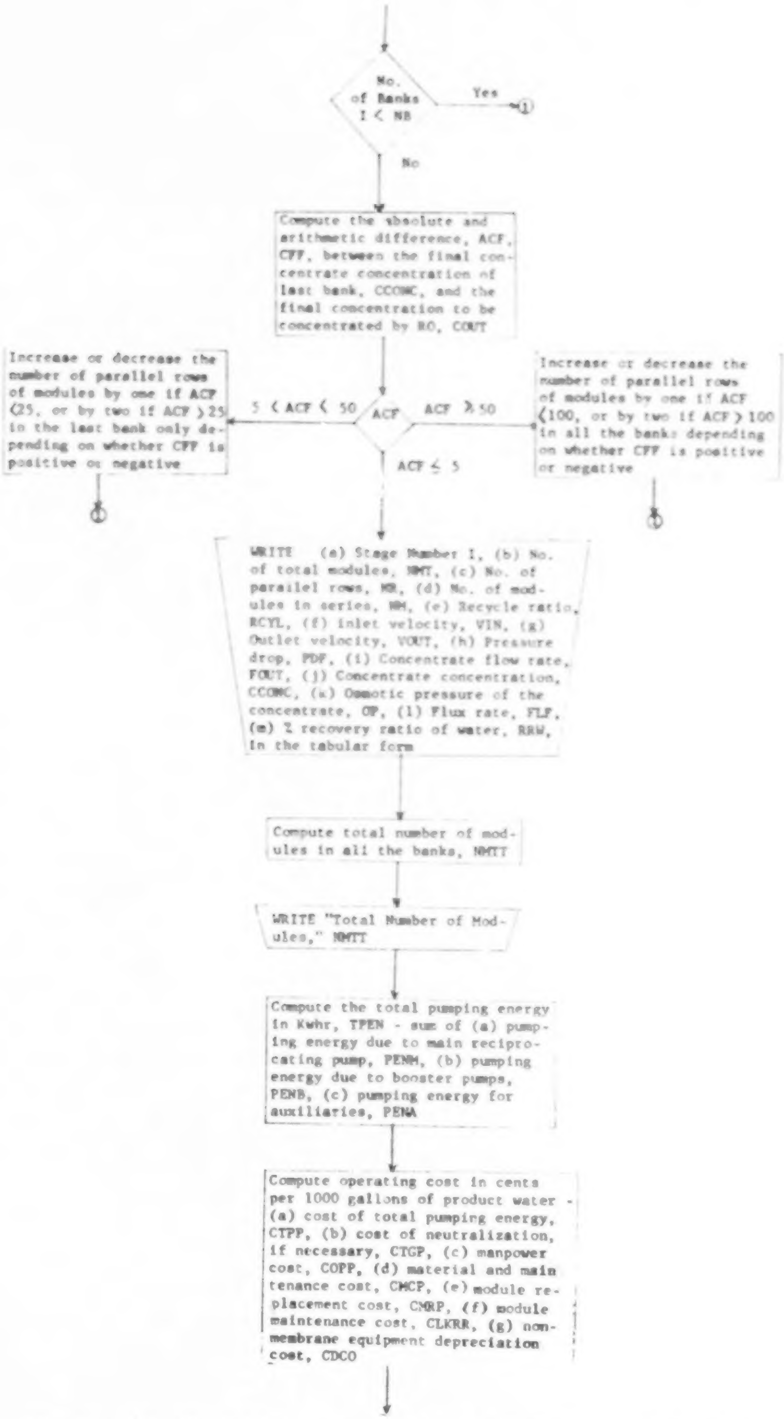

No. of Banks I < NB
Yes
①
No
Compute the absolute and arithmetic difference, ACF, CFF, between the final concentrate concentration of last bank, CCONC, and the final concentration to be concentrated by RO, COUT
ACF
5 < ACF < 50
ACF ≥ 50
ACF ≤ 5
Increase or decrease the number of parallel rows of modules by one if ACF <25, or by two if ACF > 25 in the last bank only depending on whether CFF is positive or negative
①
Increase or decrease the number of parallel rows of modules by one if ACF <100, or by two if ACF > 100 in all the banks depending on whether CFF is positive or negative
①
WRITE (a) Stage Number I, (b) No. of total modules, NMT, (c) No. of parallel rows, NR, (d) No. of modules in series, NM, (e) Recycle ratio, RCYL, (f) inlet velocity, VIN, (g) Outlet velocity, VOUT, (h) Pressure drop, PDF, (i) Concentrate flow rate, FOUT, (j) Concentrate concentration, CCONC, (k) Osmotic pressure of the concentrate, OP, (l) Flux rate, FLF, (m) % recovery ratio of water, RRW, in the tabular form
Compute total number of modules in all the banks, NMTT
WRITE "Total Number of Modules," NMTT
Compute the total pumping energy in Kwhr, TPEN - sum of (a) pumping energy due to main reciprocating pump, PENM, (b) pumping energy due to booster pumps, PENB, (c) pumping energy for auxiliaries, PENA
Compute operating cost in cents per 1000 gallons of product water - (a) cost of total pumping energy, CTPP, (b) cost of neutralization, if necessary, CTGP, (c) manpower cost, COPP, (d) material and maintenance cost, CMCP, (e) module replacement cost, CMRP, (f) module maintenance cost, CLKRR, (g) non-membrane equipment depreciation cost, CDCO

Figure 60 (Cont'd). Flow Chart of Reverse Osmosis Optimization Studies

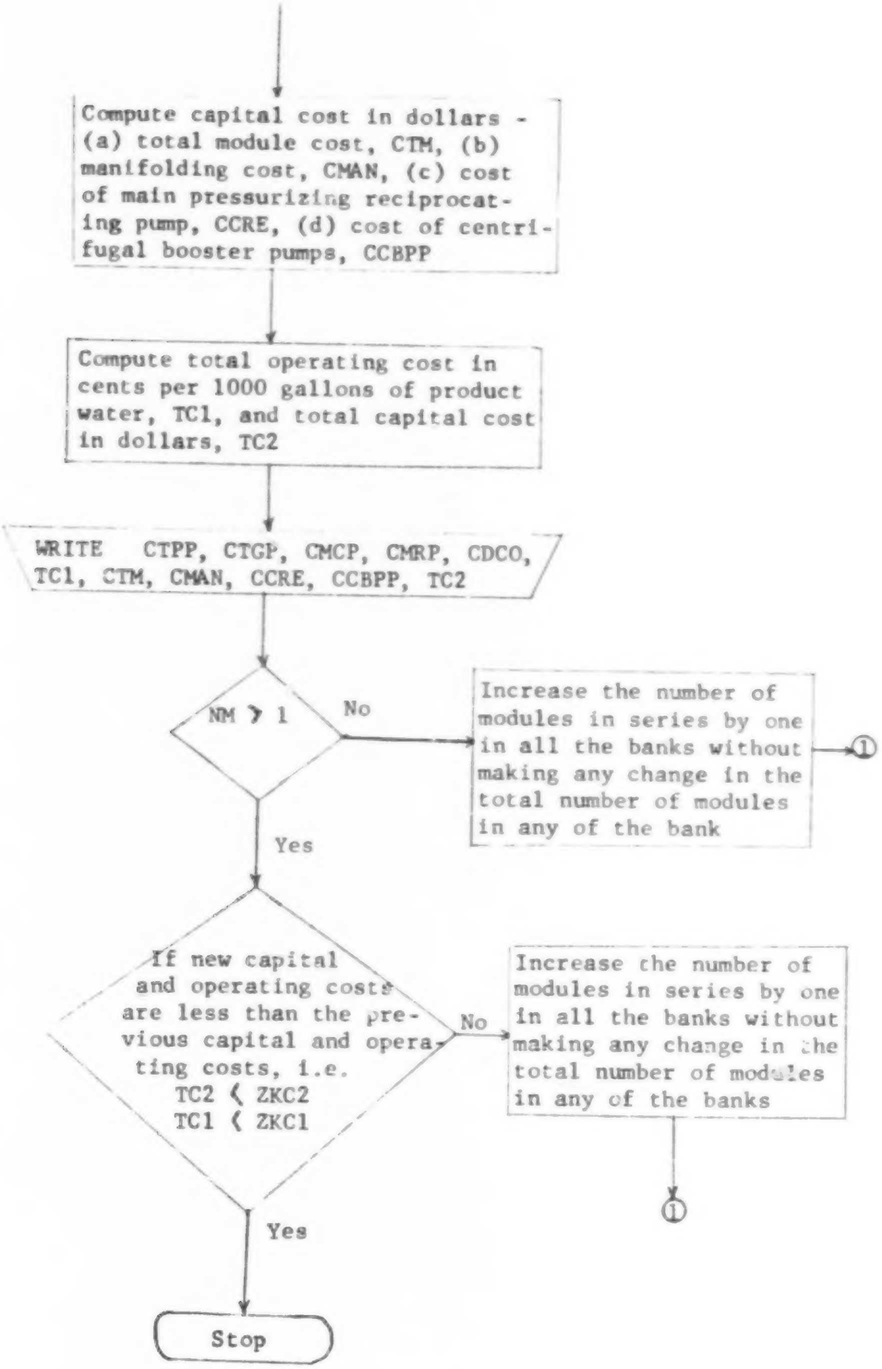

Compute capital cost in dollars - (a) total module cost, CTM, (b) manifolding cost, CMAN, (c) cost of main pressurizing reciprocating pump, CCRE, (d) cost of centrifugal booster pumps, CCBPP
Compute total operating cost in cents per 1000 gallons of product water, TC1, and total capital cost in dollars, TC2
WRITE CTPP, CTGP, CMCP, CMRP, CDCO, TC1, CTM, CMAN, CCRE, CCBPP, TC2
NM > 1
No
Increase the number of modules in series by one in all the banks without making any change in the total number of modules in any of the bank
①
Yes
If new capital and operating costs are less than the previous capital and operating costs, i.e. TC2 < ZKC2 TC1 < ZKC1
No
Increase the number of modules in series by one in all the banks without making any change in the total number of modules in any of the banks
①
Yes
Stop

Figure 60 (Cont'd). Flow Chart of Reverse Osmosis Optimization Studies

NB = Number of banks or stages
RR(I) = Approximate recovery ratios of product water in each stage
EFFE = Combined pump-motor efficiency
ARGT = Grams of neutralizing reagent per 1000 gallons of feed solution
NYRRR = Module depreciation, years
NYR = Non-membrane equipment life, years
CPEN = Cost of pumping energy, cents/Kwh
CRGT = Cost of chemical reagent, cents/lb
CMP1, CMP2 = Manpower cost ($)-unit size (gpd) relationship
CMM1, CMM2 = Maintenance and materials cost ($)-unit size (gpd) relationship
CMN1, CMN2 = Manifolding cost ($) — number of manifolds relationship
REPC, REXP = Main pressurizing reciprocating pump capital cost ($) — capacity head (gpm x psi) relationship
CPEC, CEXP = Centrifugal booster pump capital cost ($) — capacity head (gpm x psi) relationship
QCOS1, QCOS2 = Parameters of process instrumentation cost as a function of RO unit size
QSPRE = Spare number of modules expressed as percentage of minimum number of modules
QMOD = Module cost, $ per sq ft of membrane
CMODL = Module maintenance cost, $ per module per year

Fortran listing of the program is also provided. There are about [illegible] Fortran statements describing the various operations and process calculations. Various comment statements, as indicated by a prefix "C," were written at various points of the computer program describing the input and output data and other important process calculations. The FORMAT statements of the output and input data were set up in such a way as to print the important input variables and the output results in a tabular form.

Sensitivity Analysis for the Mathematical Model

The design and use of reverse osmosis as a method for concentrating pulping process effluents involves a complex, multistage, continuous system. The logical development of an accurate description of such a system, thus, becomes similarly quite complex. In dilute wastes of the pulp and paper industry, this complexity also arises from the complex character of these dilute wastes. Most of these liquors, such as NSSC liquor, have significant amounts of colloidal and of fine particulate suspended solids. These colloidal and suspended solids have a tendency to "foul" the membrane surfaces, thus resulting in poorer long-term flux rate and rejection characteristics of the membrane. To our knowledge, fouling has not been defined or explained mathematically. In order to overcome this limitation, we made systematic experimental studies for the determination of the required degrees of turbulence and mixing necessary to minimize these fouling effects.

FORTRAN PROGRAM LISTING

```
/JOB GO
/FTC LIST
BPS FORTRAN D COMPILER
          C     CASE STUDY- OPTIMIZATION CRITERION OF LARGE SCALE
          C     REVERSE OSMOSIS UNIT
 S.0001         DIMENSION NMT(100),NR(100),NM(100),RR(100),RCYL(100),VIN(100),
               1VOUT(100),PDF(100),FOUT(100),CCONC(100),OP(100),NMN(100),
               2FLF(100),RRW(100)
          C     GIVEN DESIGN CAPACITY OF REVERSE OSMOSIS UNIT,
          C     INITIAL CONCENTRATION OF THE FEED, AND THE FINAL
          C     CONCENTRATION TO BE CONCENTRATED BY REVERSE OSMOSIS
 S.0002         READ (5,1) DGD,CIN,COUT
          C     GIVEN TUBE INSIDE DIAMETER AND MODULE SURFACE AREA
 S.0003         READ (5,2) D,SA
          C     GIVEN REFERENCE PRESSURE AND REFERENCE TEMPERATURE
 S.0004         READ (5,2) AP,TEMP
          C     GIVEN REFERENCE FLUX RATE AND REFERENCE OSMOTIC PRESSURE OF
          C     SODIUM CHLORIDE SOLUTION
 S.0005         READ (5,2) FLNA,PINA
          C     GIVEN APPROXIMATE AVERAGE LIQUCR FLUX RATE AT
          C     REFERENCE PRESSURE AND REFERENCE TEMPERATURE
 S.0006         READ (5,7) AFL
          C     GIVEN EMPIRICAL CONSTANTS OF THE VELOCITY - CONCENTRATION EQUATION
 S.0007         READ (5,3) VC1,VC2
          C     GIVEN EMPIRICAL CONSTANTS OF THE OSMOTIC PRESSURE - CONCENTRATION
          C     EQUATION
 S.0008         READ (5,3) OPC1,OPC2
          C     GIVEN EMPIRICAL CONSTANTS OF THE PERCENTAGE REJECTION RATIO -
          C     CONCENTRATION EQUATION
 S.0009         READ (5,3) RRC1,RRC2
          C     GIVEN EMPIRICAL CONSTANTS OF THE PRESSURE DROP - VELOCITY
          C     EQUATION AS A FUNCTION OF CONCENTRATION
 S.0010         READ (5,4) PDC1,PDC2,PDV1,PDV2
          C     GIVEN LIMIT ON MAXIMUNM FRICTIONAL PRESSURE DROP
 S.0011         READ (5,7) PDMX
          C     GIVEN MEMBRANE COMPACTION RATE EXPRESSED IN TERMS OF THE EFFECT
          C     OF PRESSURE ON MEMBRANE CONSTANT
 S.0012         READ (5,1112) CRCAM
          C     GIVEN PERCENTAGE INCREASE IN FLUX RATE PER DEGREE CENT.
 S.0013         READ (5,7) PINF
          C     GIVEN NUMBER OF BANKS OR STAGES
 S.0014         READ (5,8) NB
          C     GIVEN RECOVERY RATIOS OF WATER IN EACH STAGE
 S.0015         READ (5,1099) (RR(I),I=1,NB)
          C     GIVEN INITIAL AND MAXIMUM NUMBER OF MODULES IN SERIES
 S.0016         READ (5,5) NZIN,NMSM
          C     GIVEN COMBINED PUMP / MOTOR EFFICIENCY
 S.0017         READ (5,7) EFFE
          C     GIVEN PUMPING ENERGY FOR AUXILIARIES EXPRESSED AS PERCENTAGE
          C     OF TOTAL PUMPING ENERGY
 S.0018         READ (5,7) PPNA
          C     GIVEN PH OF THE FEED FOR REVERSE OSMOSIS PROCESSING AND THE
          C     AMOUNT OF REAGENT USED IN GMS. PER 1000. GALLONS
 S.0019         READ (5,2) PHRO,ARGT
          C     GIVEN MODULE DEPRECIATION IN NUMBER OF YEARS
 S.0020         READ (5,9) NYRRR
          C     GIVEN NON-MEMBRANE EQUIPMENT LIFE IN NUMBER OF YEARS
 S.0021         READ (5,8) NYR
          C     GIVEN NUMBER OF PARALLEL ROWS FROM EACH MANIFOLD
 S.0022         READ (5,8) NPRM
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              C      GIVEN COST OF PUMPING ENERGY IN CENTS PER KWHR.
S.0023               READ (5,7) CPEN
              C      GIVEN COST OF REAGENT IN CENTS PER LB.
S.0024               READ (5,7) CRGT
              C      GIVEN EMPIRICAL CONSTANTS OF THE COST OF MANPOWER IN
              C      $ / YEAR - UNIT SIZE IN GPD EQUATION
S.0025               READ (5,2) CMP1,CMP2
              C      GIVEN EMPIRICAL CONSTANTS OF THE COST OF MAINTENANCE AND
              C      MATERIAL IN $ / YEAR - UNIT SIZE IN GPD EQUATION
S.0026               READ (5,2) CMM1,CMM2
              C      GIVEN EMPIRICAL CONSTANTS OF THE COST OF MANIFOLDING
              C      IN $ / YEAR - NUMBER OF MANIFOLDS
S.0027               READ (5,2) CMN1,CMN2
              C      GIVEN EMPIRICAL CONSTANTS OF THE COST IN $ - CAPACITY HEAD IN
              C      GPMXPSI EQUATION, ADJUSTING FACTOR, OPERATING LIMIT FACTOR,
              C      YEAR INDEX, AND NORMAL MODULE FACTOR FOR MAIN PRESSURIZING
              C      RECIPROCATING PUMP
S.0028               READ (5,10) REPC,REXP,RADJ,ROLF,RYIX,RNMF
              C      GIVEN EMPIRICAL CONSTANTS OF THE COST IN $ - CAPACITY HEAD IN
              C      GPMXPSI EQUATION, ADJUSTING FACTOR, OPERATING LIMIT FACTOR,
              C      YEAR INDEX, AND NORMAL MODULE FACTOR FOR CENTRIFUGAL
              C      BOOSTER PUMP
S.0029               READ (5,10) CEPC,CEXP,CADJ,COLF,CYIX,CNMF
              C      GIVEN PARAMETERS OF PROCESS INSTRUMENTATION COST AS A
              C      FUNCTION OF R.O. UNIT SIZE
S.0030               READ (5,2) QCOS1,QCOS2
              C      GIVEN SPARE MODULES EXPRESSED AS PERCENTAGE OF
              C      MINIMUM NUMBER OF MODULES
S.0031               READ (5,7) QSPRE
              C      GIVEN MODULE COST PER SQ. FT. OF MEMBRANE AND
              C      MODULE MAINTENANCE COST
S.0032               READ (5,2) QMOD,CMODL
S.0033             1 FORMAT (3F10.2)
S.0034             2 FORMAT (2F10.2)
S.0035             3 FORMAT (2E16.7)
S.0036             4 FORMAT (4E16.7)
S.0037             5 FORMAT (2I3)
S.0038             7 FORMAT (1F10.2)
S.0039             8 FORMAT (1I3)
S.0040             9 FORMAT (1I5)
S.0041            10 FORMAT (6F10.2)
S.0042          1099 FORMAT (4F10.2)
S.0043          1112 FORMAT (1E16.7)
S.0044               CMOD=(QMOD)*(SA)
S.0045               NDAY=(330.00)*(NYRRR)
S.0046               SUMM3=0.0
S.0047               NBM=NB-1
S.0048               RAP=600.00
S.0049               RTEMP=35.00
S.0050               PTF=(TEMP-RTEMP)*(PINF/100.00)
S.0051               G=(0.4087)/(D)**2
S.0052               TWR1=(1.0-CIN/COUT)
S.0053               TWR=DGD/TWR1
S.0054               F=TWR/1440.0
S.0055               AMCT=(FLNA)/(RAP-PINA)
S.0056               AMCTN=(AMCT)-(AP-RAP)*(CRCAM)
S.0057               FW=(AMCTN)*(RAP)
S.0058               WRITE (6,722) DGD,TWR,CIN,COUT,PHRC,AP,TEMP,FLNA,PINA
S.0059           722 FORMAT ('1',20X,'OPTIMIZATION CRITERION OF LARGE SCALE'/
                    130X,'REVERSE OSMOSIS UNIT'/////
```

```
          24X,'HAVENS 18 TUBE TUBULAR MODULES',
          310X,'N.S.S.C. WHITE WATER'///
          44X,'DESIGN CAPACITY OF REVERSE OSMOSIS UNIT=',
          56X,F10.1,2X,'GAL./DAY OF PRODUCT WATER'/55X,'OR'/
          643X,'=',6X,F10.1,2X,'GAL./DAY CF LIQUOR FEED RATE'//
          74X,'INITIAL CONCENTRATION OF THE FEED=',12X,F10.1,2X,'GM./L.'//
          84X,'FINAL CONCENTRATION OF THE CONCENTRATE=',
          S7X,F10.1,2X,'GM./L.'//
          T4X,'PH OF THE FEED =',31X,F10.1//
          94X,'REFERENCE PRESSURE=',27X,F10.1,2X,'PSIG'//
          X4X,'REFERENCE TEMPERATURE=',24X,F10.1,2X,'CENT.'//
          Y4X,'REFERENCE 5000 PPM SODIUM CHLORIDE SOLUTION'/
          Z4X,'FLUX RATE AT 600. PSIG AND 35. CENT.=',9X,F10.1,
          D2X,'GAL./DAY/SQ.FT.'//
          E4X,'REFERENCE OSMOTIC PRESSURE OF'/
          F4X,'SODIUM CHLORIDE SOLUTION=',21X,F10.1,2X,'PSIA')
           WRITE (6,9722) QMOD,CMODL,CPEN
     9722 FORMAT (/4X,'MODULE COST=',34X,F10.1,2X,
          1'DOLLARS PER SQ. FT. OF MEMBRANE'//
          24X,'MODULE MAINTENANCE COST=',22X,F10.1,2X,
          3'DOLLARS PER MODULE PER YEAR'//
          44X,'COST OF ELECTRIC POWER=',23X,F10.1,2X,'CENTS PER KWHR.')
           IF (ARGT-1.00) 9888,9888,6988
     6988 WRITE (6,7777) CRGT
     7777 FORMAT (/4X,'COST OF CHEMICAL REAGENT=',21X,F10.1,
          A2X,'CENTS PER LB.')
     9888 WRITE (6,9777) NYRRR,NYR
     9777 FORMAT (/4X,'MODULE DEPRECIATION=',24X,I10,2X,'YEARS'//
          74X,'NON-MEMBRANE EQUIPMENT LIFE=',16X,I10,2X,'YEARS')
          DO 55 I=1,NB
          WR=RR(I)*DGD/100.0
          CMR=WR/AFL
       55 NMT(I)=CMR/SA
          SUM=0.00
          NMI=NZIN
       65 DO 60 I=1,NB
          IF (I-1) 21,21,22
       21 FF=F
          CF=CIN
          PIF=(OPC1)+(OPC2)*(CF)
          CS=(RRC1)+(RRC2)*(CF)
          PD=0.0
          GO TO 23
       22 NBB=I-1
          FF=FOUT(NBB)
          PIF=OP(NBB)
      956 CS=(RRC1)+(RRC2)*(CF)
       23 IF (1.0-SUM) 871,172,172
      871 NI=NZXT
          SUM3=0.0
          GO TO 471
      172 NI=NMI
          GO TO 173
      171 SUM3=CM
      471 NI=NI+1
      173 NR(I)=NMT(I)/NI
          NM(I)=NI
          TFR=FF/NR(I)
          GFR=TFR
          VR=G*TFR
      VMIN=(VC1)+(VC2)*(CF)
      IF (VR-VMIN) 581,581,582
  582 RCYL(I)=0.00
      GO TO 584
  581 FR=VMIN/G
      RCYL(I)=(FR/TFR)-(1.00)
  681 RCYL(I)=RCYL(I)+0.02
      PD=0.0
  584 FR=(GFR)*(1.0+RCYL(I))
      TFR=GFR
      VR=G*FR
      VIN(I)=VR
C     CALCULATE PERMEATION RESISTANCE, FLUX RATE, AND FINAL
C     CONCENTRATION OF CONCENTRATE IN EACH SERIES MODULE
      DO 90 II=1,NI
      IF (II-1) 41,41,42
   41 TFM=FR
      CM=CF
      PIM=PIF
      TP=-(CS)/100.00
      GO TO 43
   42 PIM=(OPC1)+(OPC2)*(CM)
      CS=(RRC1)+(RRC2)*(CM)
      TP=-(CS)/100.0
      TFM=TFM-
   43 V=G*TFM
      IF (V) 361,361,362
  362 A1=(PDC1)+(PDC2)*(CM)
      B1=(PDV1)+(PDV2)*(CM)
      TT1=V**B1
      PD1=TT1*A1
      PD=PD+PD1
      PR=PIM+PD
      TLL=(AP-PR)/RAP
      TL=(FW)*(TLL)
      FL=(TL)+(TL)*(PTF)
      P=(FL*SA)/1440.0
      TFR=TFR-P
      FMM=TFR+P
      H1=TFR/FMM
      IF (H1) 361,361,382
  382 H2=H1**TP
   90 CM=H2*CM
      PDF(I)=PD
      VMIN=(VC1)+(VC2)*(CM)
      VOUT(I)=(G)*(TFM-P)
      IF (VOUT(I)-VMIN) 681,681,682
  682 IF (1.0-SUMM3) 981,981,181
  981 IF (CM-SUM3) 181,782,782
  782 IF (PDMX-PDF(I)) 181,181,171
  181 NM(I)=NI
      NR(I)=NMT(I)/NM(I)
      NMT(I)=NR(I)*NM(I)
      FOUT(I)=TFR*NR(I)
      POUT=(FF-FOUT(I))*(1440.00)
      RRW(I)=(POUT/TWR)*(100.00)
      CCONC(I)=CM
      CF=CCONC(I)
      OP(I)=(OPC1)+(OPC2)*(CF)
      PR=OP(I)+PDF(I)
      TLL=(AP-PR)/RAP
      TL=FW*TLL
      FLF(I)=(TL)+(TL)*(PTF)
  850 IF (I-NB) 853,642,642
  853 CFF=COUT-CF
      IF (CFF) 361,361,950
  950 FF=FOUT(I)
   50 CONTINUE
  642 CFF=COUT-CF
      ACF=ABS(CFF)
      IF (ACF-100.00) 68,75,75
   68 IF (ACF-50.00) 76,64,64
   76 IF (ACF-25.00) 99,109,109
   99 IF (ACF-5.00) 902,902,140
  109 JJ=2
      GO TO 53
  140 JJ=1
   53 IF (CFF) 86,102,87
   86 NR(NB)=NR(NB)-JJ
      GO TO 88
   87 NR(NB)=NR(NB)+JJ
   88 NMT(NB)=NR(NB)*NM(NB)
      NB1=NB-1
      PIF=OP(NB1)
      FF=FUUT(NB1)
      CF=CCONC(NB1)
      I=NB
      GO TO 956
  361 K=3
      GO TO 111
   75 K=2
      GO TO 105
   64 K=1
  105 IF (CFF) 111,102,112
  111 DO 113 I=1,NB
      NR(I)=NR(I)-K
  113 NMT(I)=NR(I)*NM(I)
      GO TO 65
  112 DO 114 I=1,NB
      NR(I)=NR(I)+K
  114 NMT(I)=NR(I)*NM(I)
      GO TO 65
  902 WRITE (6,9723)
 9723 FORMAT ('1REVERSE OSMOSIS OPTIMIZATION STUDIES (CONTINUED)'/)
      WRITE (6,723)
  723 FORMAT (///'STAGE',11X,'NUMBER OF',11X,'RE-',6X,'VEL.',
     15X,'VEL.',5X,'TOTAL',12X,'E F F L U E N T',13X,'0/0')
      WRITE (6,725)
  725 FORMAT ('NUM-',5X,'TOTAL',4X,'PAR-',5X,'SER-',5X,'CYCLE',4X,'IN',
     37X,'OUT',6X,'PRE-',5X,'FLOW',5X,'CONC.',4X,'OSM.',5X,'FLUX',
     A5X,'REC.')
      WRITE (6,726)
  726 FORMAT ('BER',6X,'MODU-',4X,'ALLEL',4X,'IES',6X,'RATIO',4X,
     B'(FT./',
     54X,'(FT./',4X,'SSURE',4X,'RATE',5X,'(GM./',4X,'PRE-',5X,'RATE',
     B5X,'RATIO')
      WRITE (6,727)
  727 FORMAT (10X,'LES',6X,'ROWS',5X,'MODU-',13X,'SEC.)',4X,'SEC.)',
     74X,'DROP',5X,'(GPM)',4X,'L.)',6X,'SSURE',4X,'(GPD/',4X,'OF')
      WRITE (6,728)
  728 FORMAT (28X,'LES',33X,'(PSI)',22X,'PSIA',5X,'SQFT)',
     C4X,'WATER')
      DO 655 I=1,NB
  655 WRITE (6,724) I,NMT(I),NR(I),NM(I),RCYL(I),VIN(I),VOUT(I),
     1PDF(I),FOUT(I),CCONC(I),OP(I),FLF(I),RRW(I)
  724 FORMAT (//I6,3I9,9F9.2)
      I=1
      NSTT=NM(I)
      NZ=0
      IMTT=0
      DO 4442 I=1,NB
      GOBX=RCYL(I)+1.00
      RCYL(I)=GOBX
      NZ=NZ+NR(I)
 4442 IMTT=IMTT+NMT(I)
      NMSPR=(IMTT*QSPRE)/(100.00)
      NMTT=NMSPR+IMTT
      WRITE (6,4445) IMTT,NMSPR,NMTT
 4445 FORMAT (////40X,'MINIMUM NUMBER OF MODULES=',I8//
     140X,'SPARE NUMBER OF MODULES=',I10//
     240X,'TOTAL NUMBER OF MODULES=',I10)
      DGDD=(F-FOUT(NB))*(1440.00)
      FOVAL=(DGDD)/(IMTT*SA)
      WRITE (6,4666) FOVAL
 4666 FORMAT (/40X,'OVERALL AVERAGE FLUX RATE=',F10.1,
     12X,'GAL./DAY/SQ.FT.')
C     CALCULATE COST OF TOTAL PUMPING ENERGY
      EFFF=EFFE/100.00
      PENM=(TWR*AP/EFFF)*(7.28E-6)
      PENB=0.00
      DO 9145 J=1,NBM
      PENBB=FOUT(J)*RCYL(J)
      PENB1=(PENBB*PDF(J))*(7.28E-6)
      PENB2=(PENB1/EFFE)*(1440.00)
 9145 PENB=PENB+PENB2
      PENT=PENM+PENB
      PENA=(PENT)*(PPNA/100.00)
      TPEN=PENT+PENA
      CTPN=(TPEN)*(CPEN/100.00)
      CTPP=(CTPN/DGDD)*(1.0E+5)
C     CALCULATE COST OF NEUTRALIZATION
      TAGT=(TWR/1000.00)*(ARGT/453.00)
      CTGT=(TAGT)*(CRGT/100.00)
      CTGP=(CTGT/DGDD)*(1.0E+5)
C     CALCULATE MANPOWER AND MAINTENANCE MATERIAL COST
      COP1=(DGDD)**(CMP2)
      COP=(COP1)*(CMP1)
      COPP=(COP/(330.0*DGDD))*(1.0E+5)
      CMC1=(DGDD)**(CMM2)
      CMC=(CMC1)*(CMM1)
      CMCP=(CMC/(330.0*DGDD))*(1.0E+5)
C     CALCULATE MODULE REPLACEMENT COST
      DGDP=DGDD*NDAY
      CMRE=NMTT*CMOD
      CMRP=(CMRE/DGDP)*(1.0E+5)
C     CALCULATE MODULE MAINTENANCE COST
      ALKR1=NMTT*CMODL
      CLKRR=(ALKR1/(330.0*DGDD))*(1.0E+5)
C     CALCULATE TOTAL MODULE COST
      CTM=NMTT*CMOD
C     CALCULATE COST OF MANIFOLDING
      NMAN=(NZ/NPRM)+1
      CMAN=(CMN1)+(CMN2*NMAN)
C     CALCULATE CAPITAL COST OF MAIN PRESSURIZING RECIPROCATING PUMP
      CCRE1=(F*AP)**(REXP)
      CCRE2=CCRE1*REPC
      CCRE3=CCRE2*RADJ*ROLF*RYIX
      CCRE=CCRE2*CNMF+CCRE3
C     CALCULATE CAPITAL COST OF CENTRIFUGAL BOOSTER PUMPS
      CCBPP=0.00
      DO 9163 J=1,NBM
      CCBP1=FOUT(J)*RCYL(J)*PDF(J)
      CCBP2=CCBP1**CEXP
      CCBP3=CCBP2*CEPC
      CCBP4=CCBP3*RADJ*ROLF*RYIX
 9163 CCBP=CCBP3*CNMF+CCBP4
      CCBPP=CCBPP+CCBP
C     CALCULATE PROCESS INSTRUMENTATION COST
      SURPC=TWR/1000.00
      IF (SURPC-500.00) 666,667,667
  666 GLRPC=QCOS1
      GO TO 670
  667 GLRPC=QCOS2
C     CALCULATE DEPRECIATION COST
  670 TODC=CMAN+CCRE+CCBPP+GLRPC
      DCOS1=(TODC/DGDD)*(1.0E+5)
      CDCO=(DCOS1)/(NYR*330.00)
C     CALCULATE TOTAL CAPITAL AND OPERATING COST
      TC1=CTPP+CTGP+COPP+CMCP+CMRP+CDCO+CLKRR
      TC2=CTM+CMAN+CCRE+CCBPP+GLRPC
      WRITE (6,1777)
 1777 FORMAT (////18X,'CAPITAL COST IN DOLLARS',34X,
     1'OPERATING COST IN CENTS PER'/
     275X,'1000.GALS. OF PRODUCT WATER')
      WRITE (6,3888) CTM,CTPP,CMAN,CTGP
 3888 FORMAT (///4X,'TOTAL MODULES COST=',22X,F14.1,
     15X,'PUMPING ENERGY COST=',24X,F10.1//
     34X,'MANIFOLDING COST=',24X,F14.1,
     35X,'NEUTRALIZATION COST=',24X,F10.1)
      WRITE (6,9666) COPP,CCRE,CCBPP,CMCP,GLRPC,CMRP,CLKRR,CDCO
 9666 FORMAT (/4X,'MAIN PRESSURIZING RECIPROCATING',
     129X,'MANPOWER COST=',30X,F10.1/
     24X,'PUMP COST=',31X,F14.1//
     34X,'CENTRIFUGAL BOOSTER PUMPS COST=',10X,F14.1,5X,
     4'MATERIAL AND MAINTENANCE COST=',14X,F10.1//
     24X,'PROCESS INSTRUMENTATION COST=',12X,F14.1,
     55X,'MODULE REPLACEMENT COST=',20X,F10.1//
     664X,'MODULE MAINTENANCE COST=',20X,F10.1//
```

```
         764X,'NON-MEMBRANE EQUIPMENT DEPRECIATION COST='3X,F10.1)
          WRITE (6,9555) TC2,TC1
     9555 FORMAT (///4X,'TOTAL CAPITAL COST=',22X,F14.1,
         15X,'TOTAL OPERATING COST=',23X,F10.1)
          NDIF=NMSM-NSTT
          IF (NDIF) 102,102,6569
     6569 SUM=2.00
          NZXT=NSTT
          GO TO 65
      102 STOP
          END
                    SIZE OF COMMON  00000    PROGRAM  14528
END OF COMPILATION  MAIN
```

For properly identifying the most critical parts of a mathematical model, we studied the effect of changes in the many parameters used in the model, and thus determined the relative importance of each contributing factor. The results obtained from these preliminary studies indicated the model is most sensitive to:

1. Changes in the characteristic flux rates of reference solutions of NaCl or other standard solutions at standardized reference pressures and temperatures.
2. Osmotic pressure of the liquors.
3. Frictional pressure drop-velocity relationship.
4. Velocity-concentration relationship.
5. Percentage increase in flux rate per °C.

Sensitivity analysis also showed that the rejection ratio-concentration relationship and membrane compaction rate are of secondary importance. Module depreciation, module cost per sq ft of membrane, module maintenance cost, and non-membrane equipment life are the most important factors in determining the capital and operating costs of a reverse osmosis unit, whereas the cost of pumping energy and neutralization are of relatively less importance. A separate analysis is made to study the effect of a number of stages, percentage recovery ratios of water in each stage, and the number of modules in series on the capital and operating costs, and is discussed in the latter part of the report.

EXPERIMENTAL STUDIES ON THE CONCENTRATING RUNS OF CALCIUM-BASE ACID SULFITE AND NSSC LIQUORS

Here we used our large-scale reverse osmosis trailer unit rated at 10,000 to 100,000 gallons daily for concentrating calcium-base acid sulfite and NSSC liquors by 4 to 15 times the original concentration of the feed liquor. These studies could be readily carried out with as little as 500 gallons of feed liquors by recycle of the liquor product fractions back to the feed tank. A schematic diagram of the experimental set-up is shown in Fig. 61. The feed liquor flows by gravity from a 5000-gallon stainless steel tank to a 500-gallon plastic tank from which the feed is pumped at about 20 psig to a Manton-Gaulin main pump. The main pump discharges the feed to Stage I. The concentrate from Stage I is fed directly to Stage III in a two-stage concentrating run. For a three-stage concentrating system, the concentrate from Stage I goes to Stage II first, and then to Stage III. The booster Pumps A and B are used to overcome the pressure drop and to provide a suitable recycle ratio, thus maintaining identical conditions of inlet pressure and inlet velocity in all the stages. The final concentrate from the last stage is returned through a heat exchanger for heating or cooling to maintain carefully controlled feed temperatures, and then recycles to the 500-gallon feed tank. The flow rate of permeate was measured from each stage. The total permeate of all the stages is collected and mixed in a small tank, and then drained to a 50-gallon plastic tank underneath the trailer. During the concentration run, the permeate from the 50-gallon tank flows by gravity to a 300-gallon plastic tank, and then is discarded to the sewer. Under constant concentrating conditions, the permeate mixes with the concentrate via a small centrifugal pump, and then recombined concentrate and permeate is returned through a heat exchanger.

A number of continuous concentrating runs were made with calcium-base acid sulfite and NSSC liquors. The results of these studies are discussed in detail as follows:

Concentrating Run of Calcium-Base Acid Sulfite Liquor

Here the concentrating run of calcium-base liquor was made in two stages, I and III, using Type 310 R-Series Havens 18-tube modules. These modules have been in use intermittently for 1-1/2 years. Only the booster Pump B was used for maintaining the inlet pressure and inlet velocity in Stage III the same as those of Stage I. Three concentrating runs of calcium-base liquor were made at an average velocity of 4.2 feet per second using three different modules configurations as follows:

(a) Twenty modules — 5 parallel rows of 2 modules in series in Stage I and 5 parallel rows of 2 modules in series in Stage III.

(b) Twenty modules — 4 parallel rows of 2 modules in series in Stage I and 4 parallel rows of 3 modules in series in Stage III.

(c) Twenty-one modules — 4 parallel rows of 3 modules in series in Stage I and 3 parallel rows of 3 modules in series in Stage III.

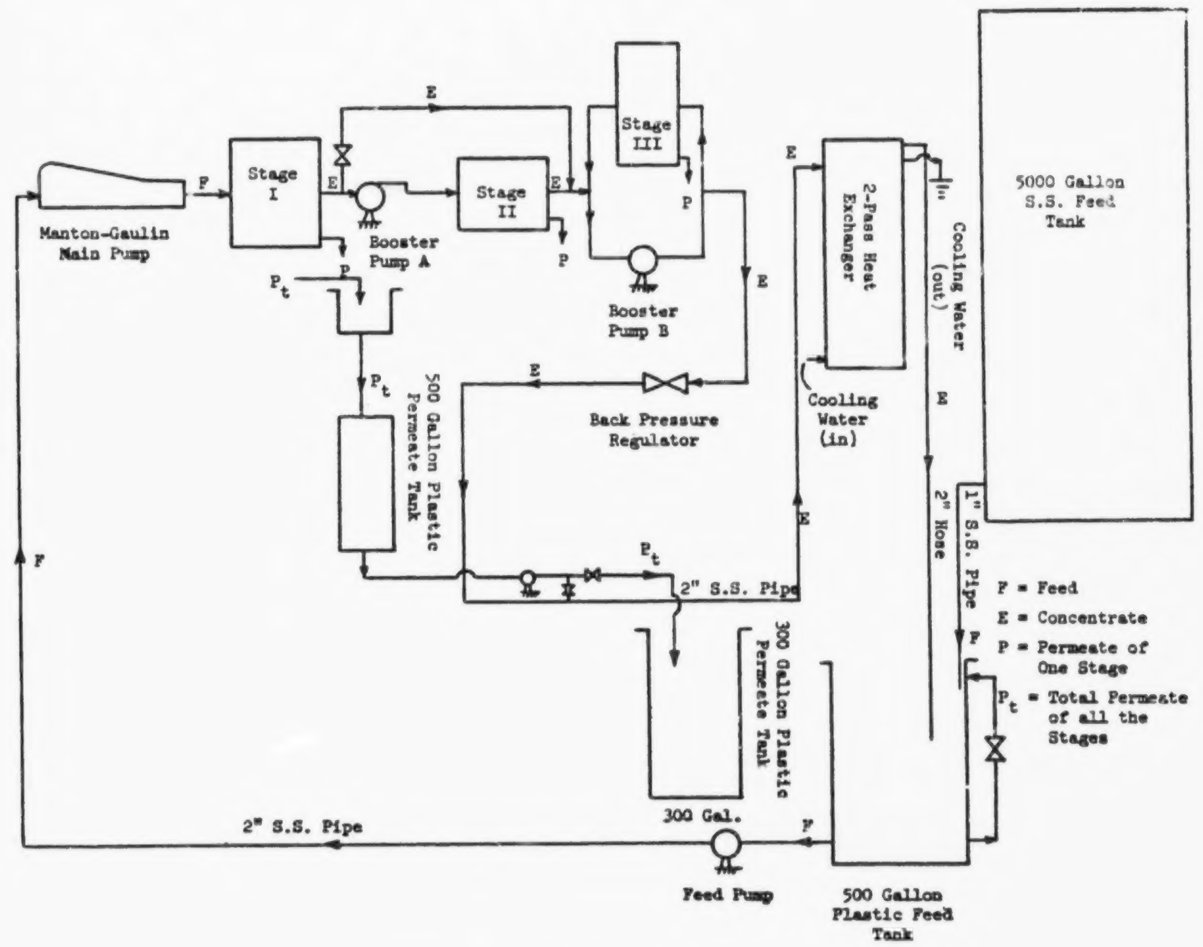
Manton-Gaulin Main Pump
F
Stage I
E
Booster Pump A
P
P
P_t
P_t
500 Gallon Plastic Permeate Tank
E
Stage II
E
P
Stage III
P
Booster Pump B
E
E
Back Pressure Regulator
P_t
2" S.S. Pipe
300 Gallon Plastic Permeate Tank
300 Gal.
Feed Pump
2" S.S. Pipe
F
F
E
2-Pass Heat Exchanger
Cooling Water (in)
Cooling Water (out)
E
E
2" Hose
5000 Gallon S.S. Feed Tank
1" S.S. Pipe
F
500 Gallon Plastic Feed Tank
F = Feed
E = Concentrate
P = Permeate of One Stage
P_t = Total Permeate of all the Stages

Figure 61. Schematic Diagram of Experimental Setup

Control flux rates on standard sodium chloride solution were measured at 4.2 feet per second before each of the concentration runs. Each flux run was made at 500 psig and 33-35°C. Before the start of each liquor run, the modules were washed with high-velocity water and with detergent BIZ solution of 15 g/l concentration. Here we concentrated calcium-base liquor only 3 times in the solids concentrations range of 10 to 42 grams solids per liter. We found we could not concentrate reliably to 10 percent solids because of greater probability of tube failure with 360 tubes in 20 of the elderly modules during unattended overnight operations.

Table 82 gives the flux rates and rejection ratios of calcium-base liquor for each of these three different modules arrangements. It is noted from Table 82 that the rejections of solids, optical density, COD, and calcium a all above 98 percent, whereas BOD_5 rejections vary between 93 and 97 percent. And the flux rates are relatively very high, on the order of 10 to 13 gfd at 500 psig and 33-35°C for 10 to 42 g/l concentrations of calcium-base liquor. These high liquor flux rates are probably due to the fact that the membrane becomes "open" after the detergent BIZ wash-up, and then calcium-base liquor forms a dynamic membrane by which the rejections are improved significantly at very little expense of flux water.

Concentrating Run of NSSC Liquor

Here dilute samples of NSSC liquors were concentrated using a recently purchased bank of the 310 Ps-Series 18-tube Calgon-Havens modules manufactured and delivered during the first 6 months of 1971. Various concentrating runs of NSSC liquors were made at an average velocity of 4.2 feet per second using two different modules configurations as shown below:

> Configuration of twenty-seven modules — 4 parallel rows of 3 modules in series in Stage I and 3 parallel rows of 3 modules in series in Stage II and 2 parallel rows of 3 modules in series in Stage III.
>
> Configuration of twenty-four modules — 5 parallel rows of 2 modules in series in Stage I and 4 parallel rows of 2 modules in Stage II and 3 parallel rows of 2 modules in series in Stage III.

The booster Pump A and B were used prior to Stages II and III for maintaining identical conditions of inlet pressure and inlet velocity in all the three stages. For each module configurations, two concentrating runs were made at two different inlet pressures of 600 and 800 psig. The sodium chloride flux rates were measured at 4.2 feet per second before each concentrating run. Each flux rate run was made under controlled conditions of inlet pressures and at 33-35°C. Before the start of each liquor run, all the modules were cleaned either with high-velocity water or with a detergent solution containing 15 grams BIZ

TABLE 82

FLUX RATES AND REJECTION RATIOS DURING THE CONCENTRATION RUN OF CALCIUM-BASE ACID SULFITE LIQUOR

(Type 310 R-Series Havens 18-Tube Old Modules)

Maximum No. of Modules = 21
No. of Stages = 2
Inlet Pressure = 500 psig
Average Feed Liquor Temperature = 33-35°C
Average Flow Rate = 2.6 g.p.m. = 4.2 ft/sec
Average 5000 mg/l NaCl Flux Rate at 500 psig and 35°C = 16.0 gfd
Rejection Ratios of NaCl = 40-70 percent

Concentration of Liquor, g/l	Flux Rate, gfd	Rejection Ratios, percent				
		Solids	OD at 281 nm	COD	BOD_5	Calcium
(a) 5 Parallel Rows of 2 Modules in Series in Stage I + 5 Parallel Rows of 2 Modules in Series in Stage III (Total Modules = 20)						
14.7	12.9	99.1	99.6	99.1	97.7	99.5
42.0	10.8	98.9	99.4	98.8	97.3	99.5
(b) 4 Parallel Rows of 2 Modules in Series in Stage I + 4 Parallel Rows of 3 Modules in Series in Stage III (Total Modules = 20)						
10.3	12.3	99.4	99.9	99.0	95.2	99.6
30.0	11.0	99.8	99.6	98.5	93.8	99.2
(c) 4 Parallel Rows of 3 Modules in Series in Stage I + 3 Parallel Rows of 3 Modules in Series in Stage III (Total Modules = 21)						
12.8	11.4	99.2	99.7	98.8	97.1	99.7
35.8	10.0	98.2	99.0	97.7	96.1	98.7

per liter. The modules during the first configuration were washed with water alone, and no detergent was used during this configuration. However, the modules during the second configuration were cleaned extensively with water and with the BIZ detergent solution. In these tests to verify the math model pulsing could not be used, yet we were able to concentrate NSSC liquors by 10 to 15 times without pressure pulsing or any kind of shutdown during any of these concentrating runs. High velocities maintained flux rates at satisfactory levels even at high solids concentrations.

Tables 83 and 84 give the flux rates and rejection ratios of NSSC liquors for two different module configurations. Figures 62A and 62B plot the corresponding flux rate vs hour of operation for these two arrangements of modules. It is noted from Table 83 that the liquor flux rate decreased from 8.3 gfd at 8.6 g/l to 3.3 gfd at 78 g/l for 600 psig inlet pressure, whereas for 700 psig, the flux rate decreased from 9.9 gfd at 6.7 g/l to 2.8 gfd at 90 g/l solids concentrations. The liquor flux as well as NaCl flux rates given in Table 84 were measured during the second module configuration and they both are relatively higher than those of Table 83. This was because the modules during the second configuration were given an extensive cleaning treatment with detergent BIZ. The data in Table 84 show that the flux rate decreased from 8.8 gfd at 9.8 g/l to 2.9 gfd at 89 g/l for 600 psig pressure, whereas for 700 psig, the flux rate decreased from 11.2 gfd at 10 g/l to 2.6 gfd at 122 g/l solids concentrations. The rejection ratios of solids, optical density, and COD were all above 95 percent, whereas sodium and BOD_5 varied between 90-95 percent, except for two permeate samples in which BOD_5 rejections were only 86-88 percent. These low BOD_5 rejections were probably due to anaerobic fermentation reactions, since we observed gas bubbles being evolved and the odor of hydrogen sulfide from these particular permeate samples.

It is to be noted that the NaCl solution flux rates for the new Ps-Series Calgon-Havens modules were very low compared to the NaCl solution flux rates of R-Series Havens old modules. These new modules had not undergone hydrolysis reactions of the cellulose acetate membrane which could increase their flux rates. Their rejections of NaCl were relatively much higher than those of R-Series old modules. The difference between the NaCl flux rates at 600 and 700 psig pressure was small and probably resulted from the membrane becoming more compacted at 700 psig. Consequently the flux rate decreased at the expense of rejections. The rejections of NaCl were found to be about 7-10 percent higher at 700 psig than the corresponding rejections at 600 psig.

Model Verification

The objective of this study was to verify the results of the mathematical model against the experimental results. One way has been to compare the flux rates of the mathematical model and experimental studies under identical conditions of module configuration, reference NaCl solution flux rate, pressure, temperature, and velocity.

TABLE 83

FLUX RATE AND REJECTION RATIOS DURING CONCENTRATION RUN OF NSSC LIQUOR
(I Module Configuration)
(Type 310 PS-Series Havens 18-Tube New Modules)

Total No. of Modules = 27
No. of Stages = 3
Set up = 4 Parallel Rows of 3 Modules in Series in Stage I + 3 Parallel Rows of 3 Modules in Series in Stage II + 2 Parallel Rows of 3 Modules in Series in Stage III
Average Feed Liquor Temperature = 33-35°C
Average Velocity = 2.5 gpm = 4.2 ft/sec
Average 5000 mg/l NaCl Flux Rate at 600 psig and 35°C = 8.0 gfd
Average 5000 mg/l NaCl Flux Rate at 700 psig and 35°C = 8.5 gfd
Rejection Ratios of NaCl at 600 psig = 70 percent
Rejection Ratios of NaCl at 700 psig = 80 percent

Concentration of Liquor, g/l	Flux Rate, gfd	Percent Rejection Ratios				
		Solids	OD at 281 nm	COD	BOD_5	Sodium
(a) Inlet Pressure = 600 psig and NaCl Flux Rate = 8.0 gfd						
8.6	8.3	98.2	99.4	98.3	97.5	97.0
30.3	6.5	97.1	99.5	97.6	95.2	95.5
54.7	4.8	96.8	99.6	97.5	94.5	94.7
78.0	3.3	95.3	99.7	96.0	93.1	92.7
(b) Inlet Pressure = 700 psig and NaCl Flux Rate = 8.5 gfd						
6.7	9.9	97.6	99.4	97.6	97.8	96.3
19.5	7.0	97.5	99.5	97.3	94.0	96.5
30.4	6.0	97.4	99.5	97.2	86.6	96.0
57.9	4.4	96.9	99.6	97.3	95.0	95.3
89.7	2.8	95.9	99.7	96.8	91.7	93.8

TABLE 84

FLUX RATE AND REJECTION RATIOS DURING CONCENTRATION RUN OF NSSC LIQUOR
(II Module Configuration)
(Type 310 PS-Series Havens 18-Tube New Modules)

Total No. of Modules = 24
No. of Stages = 3
Set up = 5 Parallel Rows of 2 Modules in Series in Stage I + 4 Parallel Rows of 2 Modules in Series in Stage II + 3 Parallel Rows of 2 Modules in Series in Stage III
Average Feed Liquor Temperature = 33-35°C
Average Velocity = 2.5 gpm = 4.2 ft/sec
Average 5000 mg/l NaCl Flux Rate at 600 psig and 35°C = 8.5 gfd
Average 5000 p.p.m. NaCl Flux Rate at 700 psig and 35°C = 1 0 gfd
Rejection Ratio of NaCl at 600 psig = 72 percent psig
Rejection Ratio of NaCl at 700 psig = 79 percent psig

Concentration of Liquor, g/l	Flux Rate, gfd	Rejection Ratios, percent				
		Solids	OD at 281 nm	COD	BOD_5	Sodium
(a) Inlet Pressure = 600 psig and NaCl Flux Rate = 8.5 gfd						
9.8	8.8	97.4	99.5	97.5	87.8	96.9
24.9	7.1	97.3	99.7	98.0	95.9	97.1
34.9	6.6	97.4	99.7	97.4	94.2	97.2
52.7	5.1	97.1	99.7	97.2	93.9	96.5
69.9	4.0	97.0	99.8	97.2	93.6	95.7
89.4	2.9	96.2	99.8	96.9	96.5	94.7
(b) Inlet Pressure = 700 psig and NaCl Flux Rate = 10.0 gfd						
10.2	11.2	97.6	99.4	98.1	95.8	95.0
27.3	9.0	97.9	99.6	98.1	95.3	95.5
34.4	8.5	97.9	99.6	98.3	98.7	96.4
47.8	7.3	97.8	99.7	98.2	95.5	96.1
75.7	5.0	97.3	99.7	96.0	97.3	95.0
121.9	2.6	95.1	99.8	96.7	93.4	92.6

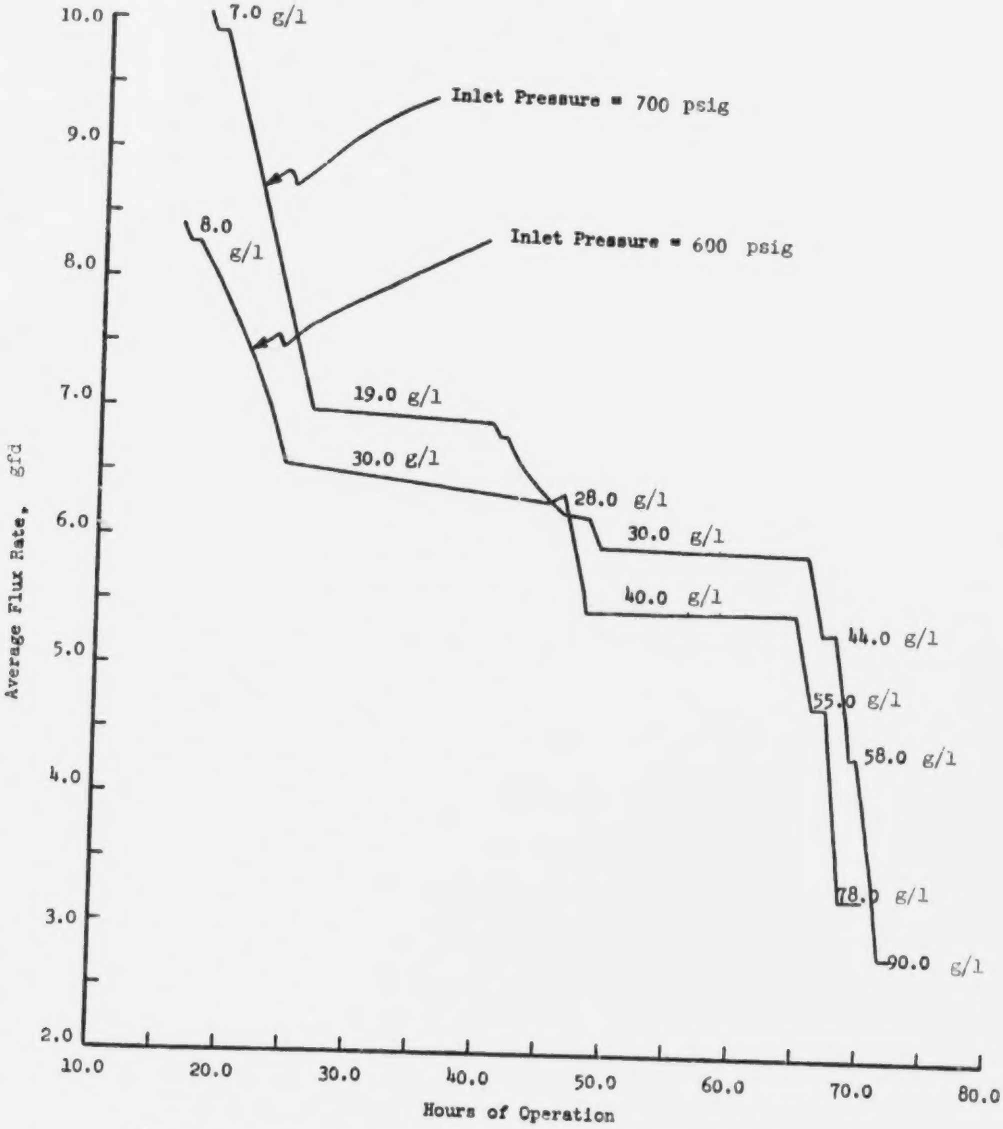

Figure 62A. Flux Rates During Concentration Runs of NSSC Liquor
(I Module Configuration)

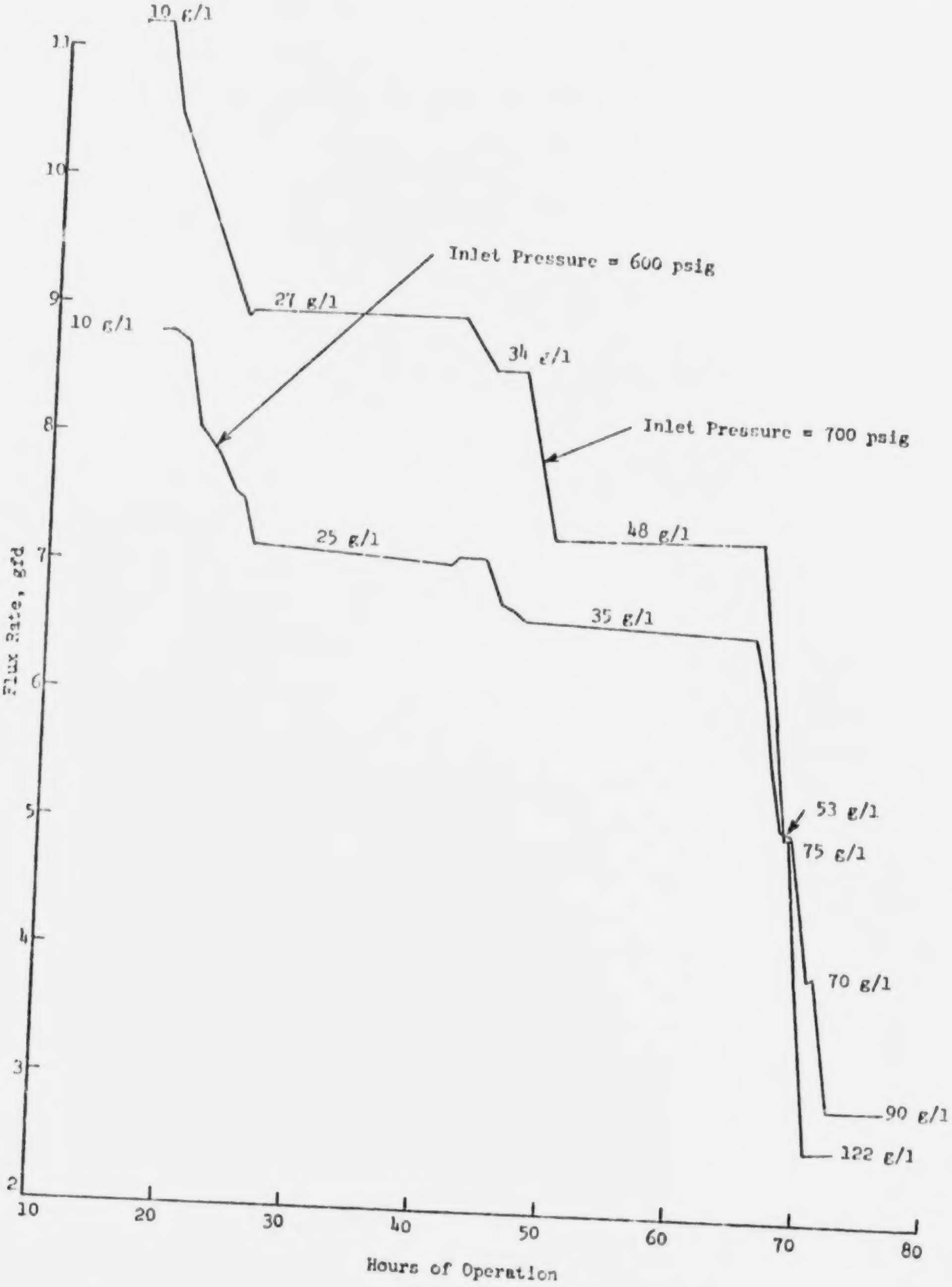

Figure 62B. Flux Rates During Concentrating Run of NSSC Liquor (II Module Configuration)

The mathematical model was run on the IBM 360, Model 44 Computer. Table 85 gives a typical computer printout of the mathematical model results for one NSSC liquor concentrating run. It is to be noted here that the mathematical model results were based on a straight-through concentrating run in which the feed was concentrated to the required solids concentration in one single throughput using a large number of modules. For experimental studies, we used a relatively small number of modules and made a concentrating run under recycling conditions. It should also be noted that the capital and operating costs of a reverse osmosis unit, as given in the computer printouts, are very approximate, and their accuracy depends strongly upon the accuracy of the input data used in the model.

Tables 86, 87, and 88 compare the experimental and mathematical model flux rates for calcium-base acid sulfite and NSSC liquors. The results of the comparative study show that the agreement between the experimental and mathematical model results was fairly good and within 10 percent. There is more than 10 percent deviation between the experimental and mathematical model flux rates for the concentrating run of NSSC liquors at 700 psig. The mathematical model flux rates are higher than the experimental flux rates. This was probably due to the fact that the reference NaCl solution flux rate, as used in the model, was not the same as was obtained experimentally. The model was very sensitive to the initial NaCl flux rate, as has been shown in the sensitivity analysis of the model.

EVALUATION OF IMPORTANT PARAMETERS FOR THE DESIGN OF MANIFOLDING AND PIPING SYSTEM OF A LARGE-SCALE REVERSE OSMOSIS UNIT

This section of the report deals with the study and evaluation of those parameters which do not depend directly upon the operating conditions, characteristics of the dilute waste streams to be processed, and the performance of the reverse osmosis membranes. These parameters are important in the design of a manifolding and piping system for the best arrangement of modules, thus minimizing both the capital and the operating costs of a reverse osmosis unit. In this study, three important parameters were considered, as follows:

Number of stages
Percentage recovery ratios of water in each stage
Number of modules in series in each parallel row

A number of computer runs were made to determine the effect of the above parameters on the total number of modules, capital and operating costs of a reverse osmosis unit. Table 89 gives the effect of the first two parameters on the total number of Calgon-Havens modules, capital and operating costs of a RO system for calcium-base acid sulfite liquor, along with the important input data used in the computer runs. It is noted from Table 89 that there is no change in the total number of modules for various combinations of recovery ratios in a 3- and

TABLE 85

OPTIMIZATION CRITERION OF LARGE SCALE REVERSE OSMOSIS UNIT

(Havens 18 Tube Tubular Modules)

NSSC White Water
Design Capacity of Reverse Osmosis Unit = 45,000.0 gal./day of product water
= 48,632.5 gal./day or liquor feed rate
Initial Concentration of the Feed = 6.7 g/l
Final Concentration of the Concentrate = 89.7 g/l
pH of the Feed = 7.8
Reference Pressure - 700.0 psig
Reference Temperature = 35°C
Reference NaCl Solution = 5000 ppm
Flux Rate at 600 psig and 35°C = 8.5 gfd
Reference Osmotic Pressure of NaCl Solution = 65.0 psia
Module cost = $9.3 per sq ft of membrane
Module Maintenance Cost = $24 per module per year
Cost of Electric Power = 1.2¢ per Kwh
Module Depreciation = 5 years
Nonmembrane Equipment Life = 5 years

Stage No.	Total Modules	No. of Parallel Rows	Series Modules	Recycle Ratio	Vel. In, ft/sec	Vel. Out, ft/sec	Total Pressure Drop, psi	Effluent				0/0 Rec Ratio of Water
								Flow Rate, gpm	Conc., g/l	Osmotic Pressure, psia	Flux Rate, gfd	
1	171	57	3	3.43	4.30	3.77	101.96	15.58	14.19	42.58	8.13	53.87
2	120	40	3	6.02	4.47	3.99	113.41	3.77	56.26	168.79	6.12	34.98
3	21	7	3	4.15	4.53	4.17	131.36	2.25	92.67	278.01	4.25	4.48

Minimum Number of Modules = 312
Spare Number of Modules = 31
Total Number of Modules = 343
Overall Average Flux Rate = 8.4 gfd

Capital Cost in Dollars	
Total modules cost	55,185.2
Manifolding cost	3,500.0
Main pressurizing reciprocating pump cost	10,700.8
Centrifugal booster pumps cost	9,143.0
Process instrumentation cost	25,000.0
Total capital cost	103,528.9

Operating Cost in Cents per 1000 Gal. of Product Water	
Pumping energy cost	10.2
Neutralization cost	0.0
Manpower cost	15.4
Material and Maintenance	5.5
Module replacement cost	73.7
Module maintenance cost	55.0
Nonmembrane equipment depreciation cost	64.5
Total operating cost	224.2

4-stage concentrating system. Also, the total number of modules do not change significantly and they indicate a maximum increase of 16 when the number of concentrating stages are increased from 3 to 4. For both 3- and 4-stage concentrating systems, the number of total modules shows a relatively larger increase of 69-85 (from 305 to 374-390) with an increase in the number of modules from 2 in series to 5 in series.

TABLE 86

COMPARISON BETWEEN EXPERIMENTAL AND COMPUTERIZED MATHEMATICAL MODEL FLUX RATES — CALCIUM-BASE ACID SULFITE LIQUOR

No. of Stages = 2

Experimental Results		Computerized Mathematical Model Results	
Concentration of Liquor, g/l	Flux Rate, gfd	Concentration of Liquor, g/l	Flux Rate, gfd
Two Modules in Series in Each Parallel Row			
14.7	12.9	22.0	11.3
42.0	10.8	40.1	10.3
Three Modules in Series in Each Parallel Row			
12.8	11.4	16.9	10.5
35.8	10.0	33.9	9.5

The results of the above studies seem to indicate that the series modules setup is a more important factor than the number of stages and in what proportions the water is removed in each stage in determining the total modules, and hence, the capital and operating costs of a reverse osmosis concentrating system. It is also noted here that we need about 305 modules (setup of 2 modules in series in each stage), rather than 395 modules with which the trailer was originally equipped, for concentrating 55,000 gallons per day of calcium-base liquor from 1.0 to 10 percent solids concentrations at 600 psig and 35°C. This run was based upon modules having a flux rate of 13.5 gfd on a control test with NaCl at 600 psig and 35°C. The bank of 305 modules was shown in the sensitivity analysis to be highly sensitive to reference NaCl flux rate.

A separate computer run was made to determine the effect of number of modules in series on the capital and operating costs of a reverse osmosis unit processing 750,000 gallons per day of NSSC liquor. The results are given in Table 90 in terms of individual items of important equipment, capital cost, and operating charges, along with the more significant input data as used in the computer run. Figure 63 plots these capital and operating costs vs number of modules in series. These cost data are interesting but they derive from a model which was developed primarily for providing comparative data but not necessarily true total installed cost for a 750,000 gallons per day reverse osmosis plant. The accuracy strongly depends upon the accuracy and completeness of the input data used in the model. Of course the relative variations of these costs with number of modules in series are quite accurate. It is noted from Fig. 63 that both the capital and the operating costs tend to become minimum for a setup of two modules in series. Therefore, two modules in series can probably be considered best for optimizing the design of a large system as based on present cost studies.

TABLE 87

COMPARISON BETWEEN EXPERIMENTAL AND COMPUTERIZED MATHEMATICAL MODEL FLUX RATES — NSSC LIQUOR
(I Module Configuration)
No. of Stages = 3
No. of Modules in Series in Each Parallel Row = 3

Experimental Results		Computerized Mathematical Model Results	
Concentration of Liquor, g/l	Flux Rate, gfd	Concentration of Liquor, g/l	Flux Rate, gfd
	Inlet Pressure = 600 psig		
8.6	8.3	14.7	6.8
30.3	6.5	31.9	6.0
54.7	4.8	82.3	3.5
78.0	3.3		
	Inlet Pressure = 700 psig		
6.7	9.9	13.2	8.2
19.5	7.0	41.8	6.8
30.4	6.0	92.1	4.3
57.9	4.4		
89.7	2.8		

TABLE 88

COMPARISON BETWEEN EXPERIMENTAL AND COMPUTERIZED MATHEMATICAL MODEL FLUX RATES - NSSC LIQUOR (II MODULE CONFIGURATION)

No. of Stages = 3

No. of Modules in Series
in Each Parallel Row = 2

Experimental Results		Computerized Mathematical Model Results	
Concentration of Liquor, g/l	Flux Rate gfd	Concentration of Liquor, g/l	Flux Rate gfd
Inlet Pressure = 600 psig			
9.8	8.8	17.2	7.7
34.9	6.6	38.3	6.6
69.9	4.0	95.9	3.6
89.4	2.9		
Inlet Pressure = 700 psig			
10.2	11.2	18.0	9.1
27.3	9.0	41.5	7.9
47.8	7.3	128.0	3.5
121.9	2.6		

TABLE 89

EFFECT OF NUMBER OF STAGES AND RECOVERY RATIOS OF WATER ON THE CAPITAL AND OPERATING COSTS

(Calgon-Havens 18-Tube Tubular Modules)

Feed Liquor = Calcium-Base Acid Sulfite Liquor
Design Capacity of Reverse Osmosis Unit = 50,000 gal./day of Product Water
or
= 55,000 gal./day of Liquor Feed Rate
Initial Concentration of the Feed = 10 g/l
Final Concentration of the Concentrate = 100 g/l
Inlet Pressure - 600 psig
Reference NaCl = (5000 ppm)
Flux Rate at 600 psig and $35^{\circ}C$ = 13.5 gfd
Module Cost = $9.3 per sq ft of membrane
Module Maintenance Cost = $24 per module per year
Cost of Electric Power = 1.2c per Kwhr
Module Depreciation = 5 years
Non-membrane Equipment Life = 5 years

Total No. of Stages	No. of Modules in Series in Each Stage	Percent Recovery Ratios of Water in Each Stage	Minimum No. of Modules in Each Stage	Total No. of Modules[a]	Overall Average Flux Rate gfd	Total Capital Cost, dollars	Total Operating Cost, cents per 1000 gallons of product water
3	2	22.6 22.3 45.7	66 66 146	305	10.5	98,112	197.5
	2	22.6 44.2 23.8	66 132 80	305	10.5	99,363	199.1
	2	45.1 19.8 25.8	132 60 86	305	10.5	97,556	196.9
	3	21.7 21.5 47.3	66 66 162		9.9	101,060	202.7
	3	21.7 42.4 26.5	66 132 96	323	9.9	101,642	204.2
	3	43.2 19.0 28.4	132 60 102	323	9.9	99,592	201.8
	4	22.7 22.3 45.3	72 72 168	343	9.3	103,504	210.1
	5	20.2 20.7 49.8	70 70 200	374	8.6	108,597	220.0
4	2	31.5 12.8 17.2 29.0	92 38 52 96	305	10.5	97,212	196.6
	3	29.6 9.5 16.3 35.0	90 36 51 123	330	9.7	100,334	204.1
	4	31.5 9.8 18.2 31.1	100 44 60 120	356	9.0	104,747	212.9
	5	31.5 7.0 18.8 33.4	105 45 65 140	390	8.2	110,617	224.6

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[a] Includes 10 percent spare modules over minimum number required for effective processing of feed loading.

TABLE 90

EFFECT OF NUMBER OF MODULES IN SERIES ON THE CAPITAL AND THE OPERATING COSTS OF REVERSE OSMOSIS UNIT

(Calgon-Havens 18-Tube Tubular Modules)

Feed Liquor = NSSC White Water
Design Capacity of Reverse Osmosis Unit = 675,000 gal./day of Product Water
or
= 750,000 gal./day of Liquor Feed Rate

Initial Concentration of the Feed = 10 g/1
Final Concentration of the Concentrate = 100 g/1
Inlet Pressure = 600 psig
Feed Liquor Temperature = 35°C
Reference Sodium Chloride (5000 ppm) and Flux Rate at 600 psig and 35°C = 13.5 gfd
Module Cost = $9.3 per sq ft of Membrane
Module Maintenance Cost = $24 per Module per Year
Cost of Electric Power = 1.2¢ per Kwh
Module Depreciation = 5 Years
Non-membrane Equipment Life = 5 Years
Number of Concentrating Stages = 3

			Capital Cost, dollars						Operating Cost in Cents per 1000 Gallons of Product Water							
No. of Modules In Series	Total No. of Modules[a]	Overall Average Flux Rate gfd	Module Cost	Mani-folding Cost	Main Pressurizing Reciprocating Pump Cost	Booster Pump Cost	Process Instrumen-tation Costs	Total Costs	Manpower Cost	Material & Maintenance Costs	Neutrali-zation Cost	Pumping Energy Cost	Replace-ment Cost	Module Maintenance Cost	Nonmembrane Equipment Depreciation Cost	Total Cost
1	3357	12.9	540,107	101,800	40,967	32,703	50,000	76[illegible],577	3.7	2.4	0.0	9.0	48.2	36.0	20.1	119.4
2	3586	12.0	576,951	54,400		37,421		759,739				9.0	51.7	38.5	16.21	121.7
3	3818	11.3	614,777	38,600		41,388		785,232				9.0	55.0	41.0	15.3	126.5
4	4074	10.6	655,465	30,900		44,521		821,853				9.0	58.7	43.8	14.9	132.6
5	4372	9.8	703,410	26.600		47,674		868,651				9.0	63.0	47.0	14.8	139.9
6	4745	9.1	763,422	24,000		50,241		928,630				9.0	68.4	51.0	14.8	149.3

[a] Includes 10 percent spare modules over minimum number required for effective processing of feed loading.

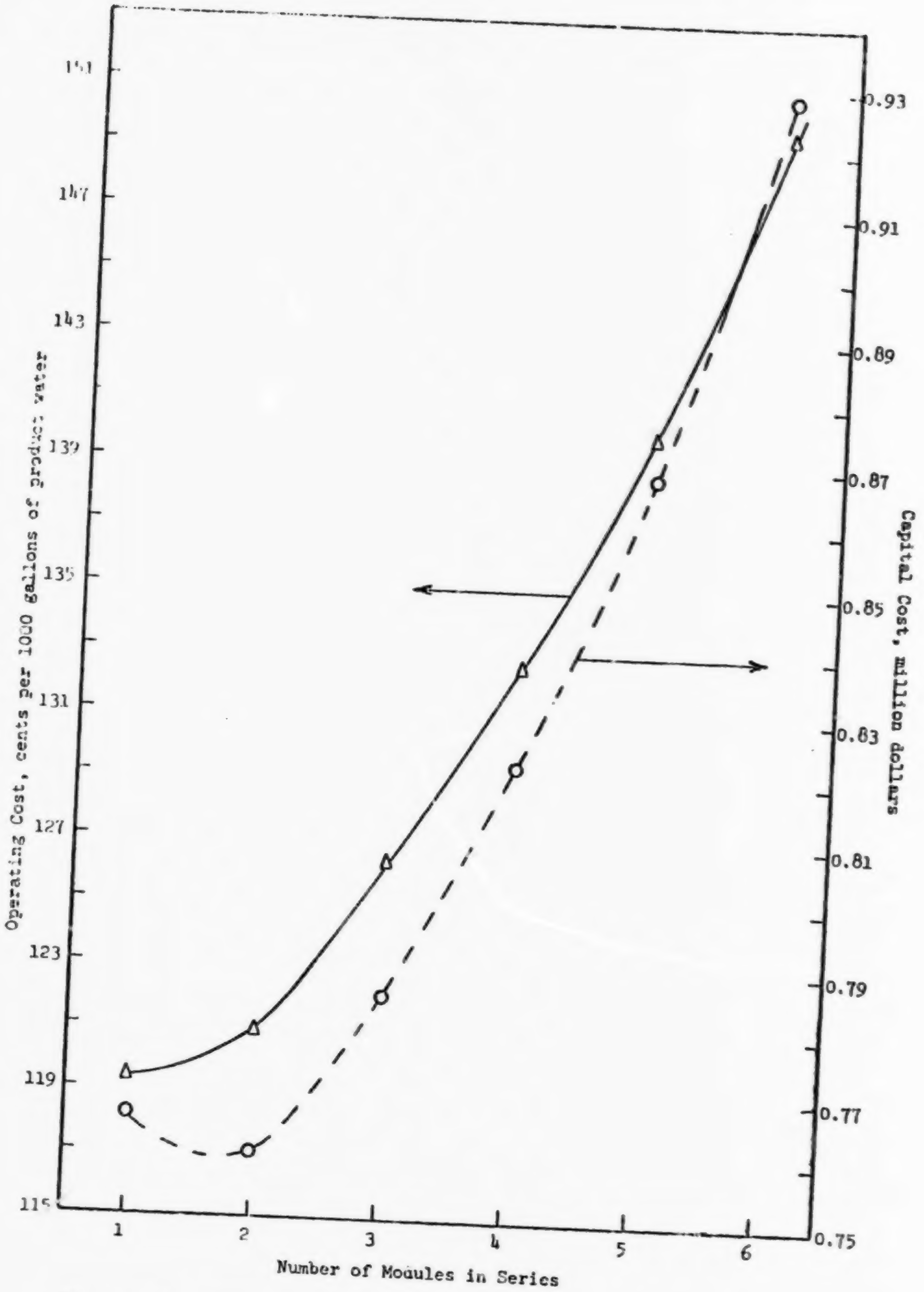

Figure 63. Effect of Number of Modules in Series on the Capital and Operating Costs of a Reverse Osmosis Unit Processing 750,000 Gallons per Day of NSSC Liquor.

CONCLUSIONS

The mathematical model developed in this study proves to be most sensitive to the reference NaCl flux rate, the osmotic pressures of the liquors being processed, module membrane life, and module and membrane replacement costs.

There is a fairly good agreement between the liquor flux rates of the mathematical model and that obtained from the experimental studies. The agreement was within 10 percent.

The number of modules in series appears to be a more important consideration than the number of stages and the recovery ratios of water in each stage in the design of the manifolding and piping system. Probably two modules, 18 tube (288 linear ft) in series is the best number based on the present capital and operating costs of an RO concentrating system.

SECTION IX

MEMBRANE MODULE LIFE STUDIES

The economics of reverse osmosis processing are critically dependent upon the life expectancy for the membrane system, as well as upon the membrane performance in terms of flux rates and solute rejections. In order to develop data for the economic study to be discussed in Section X, detailed records were maintained throughout this project for the purpose of establishing the life history of the membrane equipment used. Additional experimental programs specifically designed to develop membrane life experience were conducted where possible within the 3-1/2 year program. Limitations on the number of life study runs which could be conducted on a sustained basis prevailed in terms of availability of reliable, continuously operated, high pressure, pumping equipment and also of manpower for detailing such studies. Nevertheless, substantial experience was gained toward this objective.

Most suppliers have indicated a 2-year life to be a major goal of membrane research and development programs and of membrane manufacturing quality control in the 1966-1971 period of development. Unless substantial values can be recovered, the economics of waste processing by RO appear questionable if membrane module replacement is required more frequently than once each two years. Laboratory studies and some isolated instances of field experience may lend confidence to projections for life expectancies at that level and may even extend to three years or more. However, actual experience in this research and demonstration project and also that of analogous field trials by others, of which the authors are aware, indicate the average life expectancy in terms of a statistically significant number of modular units of membrane equipment manufactured in 1970 or before has yet to be adequately proven out at the one-year level. The time lag in developing well-controlled and reliable data is an obvious obstacle to drawing conclusions as to the life expectancy of newly designed or improved equipment recently introduced to the market.

The 387 modules with which the large trailer unit was originally equipped were of 1967 design and were manufactured early in 1968. Two hundred sixty of these were rebuilt at the factory a year later in September 1969 after somewhat less than 2000 hours of actual service under full pressure. Important improvements have since been made, and several new types or modifications have issued from this manufacturer in 1970 and 1971. Similar model changes and improvements are apparent for equipment being offered by all suppliers active in the field throughout the period of conducting this research and demonstration project.

The laboratory and small pilot scale life expectancy runs were planned and conducted to supplement the experience on the large trailer-mounted field unit. Specific problem areas affecting life performance of membrane modules exposed to service conditions in concentration processing

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of pulp and paper industry effluents could best be evaluated in this manner. Those conditions for waste treatment proved to be a severe test and the results were substantially less than required for meeting minimum standards of economic feasibility in large-scale commercial operations.

Data being accumulated in studies continuing after terminating this specific Research and Demonstration Project which is subject for this report may be expected to show continuing progress being achieved toward extending membrane and module life beyond the minimum 12-month goal and on toward the more favorable 2- and 3-year life levels.

Equipment

Most of the various laboratory and pilot test stands, and also the large trailer-mounted field unit as described in Sections V, VI, and VII have at times been employed individually and collectively in these membrane module life testing studies. Reliability of high pressure pumps was a first problem. It took some patience and much "doing" to maintain the several rotary piston pumps available for early studies in around-the-clock, 7-day week service, but the pilot plant crew, with the help of the laboratory staff and group leaders, maintained a night and day "on call" program with remarkable loyalty and perseverance. Later, the larger Milton Roy variable stroke, positive displacement, piston pumps became available especially for sustained and continuous research service and less out of hours attention was required. At least one such life study has been under way at all times within this project in the 4-year period, 1966 through 1971, and as many as four units have been operating simultaneously at times on the various types of equipment supplied for testing by cooperating manufacturers.

Much of the exploratory testing involved a range of the types and kinds of membrane modules becoming available and was made possible by loan of equipment without charge by a number of manufacturers developing modified designs for waste treatment as well as for salt water conversion service. Such equipment is described by type but the cooperating suppliers are not specifically identified. Cooperating concerns are listed in the appendix.

Methods

The pattern for life testing utilized pumping test stands described in detail in prior sections of this report. Each unit was complete with automated instrumentation and controls employing a system of relays and timers to maintain system temperatures, pH and pressure levels. These sensors were integrated with automated shutoffs to the pump power supply in case of failures. The timers operated pulsing systems (temporary programmed release of pressure for short periods of 30 seconds to several minutes every hour or so) to control fouling and also were used at times for control of periodic changes in feed flows and the like.

The feed systems usually could be maintained on a continuous, straight-through basis in field tests at the mills where adequate supplies of fresh liquor were available continuously or where feed tanks could be filled periodically during the day. The Appleton laboratory and pilot plants have tanks available for up to 10,000 gallons feed storage. This capacity was used for several test runs of limited duration, utilizing truck load quantities but usually the life testing on the Institute campus was carried out with recycle of 50 to 500-gallon quantities of test solution made up in batches and replaced at suitable intervals. Both permeate and concentrate product flows were returned and mixed to provide a continuous supply of feed liquor.

Most of the principal pulping and bleaching effluents meriting specific studies were subjected to testing in the life test studies. But the standard test solution for routine studies was made up at a solids concentration of 1 percent by diluting 50 percent Ca-base spent sulfite liquor concentrate (commercially available as "lignin liquor" under various trade names). This "standard" feed liquor, approximating a principal type of pulp wash water, has been the principal comparative test solution used for these life test evaluation studies. Other specific pulp wash waters and bleach liquors have been subject for extended studies when the logistics of supply permitted.

Analytical control for the life tests necessarily had to be based on the minimum expenditure of man hours for measuring, sampling, and conducting control assays necessary in maintaining a continuous record on performance of membrane units under life tests. For most of the runs reported, feed flows were routinely metered by use of the positive displacement piston pumps with adjustable stroke length. Six individual Milton Roy pumps, three of which were purchased especially for this project, provided infinitely variable flows with reproducible stroke length adjustment, and were selected for this purpose in flow capacities up to 3 to 5 gallons per minute each. Permeate flows were taken periodically during each day from several individual modules, and wherever possible from banks of two or more modules to obtain statistically sound, averaged data. Temperature and pH could be recorded automatically at times, and where necessary, but availability of such facilities was necessarily limited. More usually the temperature was controlled within desired limits without recording, and the pH in feed tanks was manually adjusted at suitable periods as needed. Pressure control was usually maintained with manually adjusted back pressure valves (Cash Acme K-20 valves on lab and small pilot units). This was not an ideal system of pressure regulation for unattended, around-the-clock operations, but worked with fair reliability at reasonable cost if the valve seats were maintained in good condition and free of plugging by suspended solids.

Life testing for the 387 modules on the large trailer-mounted unit was a special objective during each of the first three field trials. Later this large unit was moved to Appleton for special studies which helped to advance the program for evaluating life expectancy. A card file with records of performance for individual modules was maintained in as much detail as could be accomplished with available manpower.

Life Test Data for Various Membrane Module Systems

Capillary Fiber

Several capillary fiber test modules were submitted for research evaluation, and the data and results were interesting in the limited areas of life study actually conducted on these units. However, no extended life testing could be achieved with the early types of test units available. Susceptibility to plugging by suspended solids contained in the feed liquor, by precipitates and crystalline deposits which developed during concentration, or by sliming as a result of microbiological cell growth, comprised problems which were not satisfactorily solved in these early tests. Sustained life studies could not be gotten under way. Several major chemical concerns are understood to be actively advancing the technology for use of the hollow fiber systems since the time these initial tests were conducted. Although plugging was a serious problem, no failures of the membrane structural support system occurred and no leakages of connections were experienced.

Sheet Membrane Pack Systems – Spiral Wound

Problems with plugging by suspended solids contained in the pulp mill effluent feed liquors or precipitates and the like which formed during operation were also apparent with the sheet membrane pack systems, such as the spiral wound module as discussed in Section V. This plugging adversely affected the development of sustained operation, and therefore made life studies dependent upon selecting feed liquors free of suspended solids or use of test solutions which could feasibly be clarified by such methods as filtration at the 3 to 10 nm level. With these prerequisites taken care of, it was possible to conduct limited, small-scale life study tests on spiral wound modules.

Three modifications of spiral wound assemblies were tested:

1. A Schedule 80 PVC tube containing two spiral wound modules with a total membrane area of 6.8 square feet and a maximum operating pressure of 400 psig.

2. Two 2-1/2 inch Schedule 80 stainless steel tubes containing ten spiral wound modules, each tube with a membrane area of 69 square feet and capable of operating at 600 psig.

3. Succeeding studies were conducted utilizing spiral wound modules of a modified type with larger than standard openings in the mesh separator to minimize plugging of the flow channel.

The PVC tube with two spiral units was intended for use in several preliminary trials to evaluate plugging problems prior to exposing the larger, more expensive stainless steel units to the process stream.

The PVC unit was installed on a test stand with a variable stroke pump and auxiliary equipment to maintain an operating pressure of 350 psig while processing a Ca-base sulfite pulping wash water that had been defibered through a 100-mesh screen.

The unit was operated five days a week for a total of eight weeks (618 hours), with weekly backwash to maintain the open flow channels. During this period there was no indication of plugging. This was a substantial improvement over earlier laboratory experience with standard modules having less space between membrane flow channels.

After eight weeks of operation at 350 psig, the PVC unit was replaced. The two larger stainless steel units were installed for operation at 600 psig. These were operated successfully for six weeks. At that time the high pressure pump had to be diverted to other test programs, so it was necessary to terminate studies on these spiral modules until a pump could again be made available.

The data tabulated in Table 91 for these two tests show the flux rate declined to some extent, but this appeared to be stabilizing at approximately 8.9 gfd during the last four weeks of operation. Rejections averaging on the order of 96 percent solids, 99 percent color, 88 percent biochemical oxygen demand (5 day), 95 percent for chemical oxygen demand, and 99 percent for calcium were achieved while processing this waste stream.

At the time of the unavoidable shutdown, unrelated to performance of the spiral equipment, a note was made in the records that "these modules should be put back into use as soon as practical, since the results look too good to warrant premature termination of the study." Unfortunately, due to pressure of other work, the processing of this stream with spiral wound modules could not again be undertaken for several months. When the modules were tried again (in late 1969), they were found to be fouled and plugged by growth of microbiological slime during storage. Incomplete washing and improper storage conditions were apparent, and replacement of the spiral modules was required.

The rebuilt modules were put back in service for a study of processing an evaporator condensate, and performed satisfactorily for more than 2000 hours. The system for control of pH failed at 2131 hours, allowing a rise to above 10, which damaged the membranes and ended the tests on these units.

A third system was provided by a different supplier of spiral wound equipment. This consisted of a newly designed wide-channel spiral wound module, a multistage centrifugal pressure pump and a preset orifice for 450 psig pressure operation. This unit was used to concentrate

TABLE 91

FLUX RATES AND PERMEATE QUALITY WITH SPIRAL WOUND MODULES ON LIFE STUDY

essing an Acid Sulfite Wash Water
(2 Gallon/Minute Flow Rate)

Week	Flux, gfd at 25°C	Feed Solids, g/l	pH		Rejection, percent				
			Feed	Permeate	Solids	OD	BOD_5	COD	Calcium
		Two Modules at 350 psig Operating Pressure							
1	6.2	13.7	4.3	3.[illegible]	98	98	90	97	98
2	6.5	10.0	4.4	3.6	96	99	92	97	99
3	6.8	14.0	3.3	2.9	95	99	90	96	99
4	6.3	12.9	4.7	3.7	97	99	91	97	99
5	6.2	12.4	3.4	3.4	96	99	90	96	99
6	4.8	15.0	4.3	3.8	97	99	89	96	99
7	5.1	12.7	4.8	4.3	98	99	87	95	99
8	5.0	12.7	3.6	2.8	95	99	89	96	99
		Twenty Modules at 600 psig Operating Pressure							
9	12.9	12.2	4.2	3.0	97	99	87	95	99
10	10.7	10.8	4.3	4.0	97	99	86	95	99
11	9.0	12.5	3.1	2.9	95	99	88	95	99
12	10.4	13.7	3.6	3.2	96	99	88	96	99
13	9.6	11.7	3.9	3.3	96	99	86	96	99
14	8.2[a]	11.2	4.7	4.2	98	99	84	94	99

[a] At 1.2 gpm flow rate.

NSSC "white water." The liquor was pretreated by passage through a 50 μm filter. The waste stream, containing a high content of suspended solids in a near colloidal state, had been tried unsuccessfully in several narrow-channel modules. The newest design, however, was thought to be less apt to plug with particulate matter, and the pulseless operation of the centrifugal pumping system warranted investigation in comparison with the pulsing normally used on this feed in tubular systems.

A flux loss of 45 percent (from 12.7 to 7.0 gfd) was experienced in the first three days of operation, followed by complete plugging of the 50-nm feed filter. Subsequently, the spiral module plugged irreversibly after the filter was removed upon the suggestion of the manufacturer.

The rejection of solids, BOD_5, COD, and color were on the order of 92-99 percent (Table 92). The flux rate deteriorated to less than one gfd at 6 percent solids and could not be restored. The unit was then returned to the manufacturer.

The laboratory and small field-scale runs on spiral wound modules demonstrated that:

1. Early designs of the spiral wound module tended to plug with suspended particulate matter, by precipitates which formed during concentration of some pulping effluents, and also by microbiological sliming.

2. Tests on clear feed streams, such as evaporator condensates, indicated the spiral units could be used satisfactorily for concentration in the range of 1 percent to 10 percent solids, and with good (90 percent or better) rejections if problems with formation of suspended solids and microbiological slime could be avoided.

3. The newest "open path" spiral modules presented no mechanical plugging problems during a 2131-hour concentrating study with an acid sulfite evaporator condensate. However, as with all units equipped with cellulose acetate membranes, they could not tolerate pH levels much above 7.5, and failure occurred when the pH control allowed the pH of the feed to rise to higher levels.

4. There was indication of microbiological fouling (slime formation) in the study with recycling feed, but properly controlled straight-through feeding of fresh substrates with periodic cleanups at intervals of about 1 week would be expected to minimize or eliminate this problem.

5. Although module failure by plugging and fouling was a serious problem with the spiral-wound sheet membrane system, there was at no time any evidence of structural failure in the membrane support system nor were leakages experienced in the connections within or outside of the well-designed module.

TUBULAR MODULES

The tubular modules evaluated in these laboratory studies were of three basic classes:

1. Replaceable modules, where failure of individual membrane or support tube components required the replacement of the entire module as a unit.

2. Replaceable tubes within a module in which the individual support tubes, complete with membranes could be replaced if membrane or tube failures occur.

TABLE 92

FLUX RATES AND PERMEATE QUALITY WITH SPIRAL WOUND MODULES ON LIFE STUDY

Processing NSSC White Water at 450 psig Operating Pressure

Hours	Flux, gfd at 25°C	Feed Solids, g/l	Rejection, percent			
			Solids	BOD_5	COD	Optical Density
			Liquor Fed to Slowly Concentrate			
3	12.7	9.5	3	92	96	99
72	7.0	9.6	99	93	96	99
168	3.8	10.3	99	93	97	99
306	2.0	22.5	99	95	96	99
			Liquor Fed to Rapidly Concentrate After Adjusting the Volume to 50 Liters with a 1 Percent Solids Liquor			
326	2.3	12.0	98	--	--	--
423	1.6	30.2	99	92	97	98
428	2.2	40.3	99	91	98	99
433	1.1	65.9	99	--	98	99
437	0.4	86.6	98	94	98	99
439	0.3	103.8	98	92	98	99
444	0.1	127.4	95	89	96	99

3. Replaceable membranes based upon membrane inserts within individual tubes which could be replaced if the rejection or flux characteristics became unacceptable.

These basic tubular designs could be further differentiated into porous and non-porous support tube structure, and the porous support styles into spiral wrapped, braided, or woven fiberglass and resin-bonded sand core types.

Identification according to the number of tubes per module could also be used as a means for classification. In order to simplify presentation of the data, discussion, and conclusions of the experimental work in this section, the headings used are in terms of the number of tubes per module for each design. Additional descriptive information has been included under each heading where required to classify the type of module under study.

Each tubular system (spiral wrapped, braided, woven fiberglass and the sand core) was evaluated, as in the case of the spiral wound module study for the total operating hours during which acceptable rates and quality of product water were maintained, as evidenced by the rejection of solids, biochemical oxygen demand, chemical oxygen demand, and color constituents from a recycled 0.5-1 percent solids pulp wash water reconstituted from a 50 percent concentrate of calcium-base acid sulfite pulp liquor. Special operating conditions of pressure, temperature, fluid velocity, and other process modifications are also discussed under the individual headings as they apply.

Seven-Tube Modules

Studies on the life of tubular units first began in December 1966 with ten of the early prototype designs available at that time. These were 7-tube modules of the spiral wrapped design and had the tubes cast permanently in resin heads. They were evaluated on a test stand comprising a rotary type, four piston pump, a 50-gallon plastic drum reservoir for the recycling liquor, and a pressure regulating valve set at 600 psig.

As the study progressed it became apparent that some modifications to the pumping equipment and controls would be necessary to provide acceptable process control. These included:

1. The installation of a stainless steel cooling coil (sixth day) to control rising temperatures due to conversion of mechanical energy into heat in the recycle system.
2. A vertical one-inch diameter 6-foot long section of stainless steel pipe as an improvised accumulator chamber was installed immediately after the pump outlet (56th day) to reduce the sharp pressure pulsations from a range of about 125 psig per stroke to about 25 psig.
3. Still another change occurred at the 174th day with placement of a forepump (Centrifugal, 18 psig maximum 20 gpm) ahead of the main pressurizing pump in an attempt to further reduce the "hammer" of sharp pressure fluctuations from the reciprocating piston pump available for these early stage evaluations.

During the 60-week test period the product water quality from intact (leak-free) modules was excellent (Table 93). The flux rates varied with the age of the module, the temperature of operation, and the condition of the membrane surface.

TABLE 93

FLUX RATES AND REJECTIONS FOR SEVEN-TUBE MODULES ON LIFE STUDY

Processing 1 Percent Acid Sulfite Wash Water

Week	Stream	Flux, gfd at 25°C	pH	Solids, mg/l	BOD_5, mg/l	Optical Density[a] at 281 nm	Color CoPt
1	Feed		5.6	5644	1608	42.5	---
	Permeate	13.8	5.3	115	845	0.56	---
5	Feed		4.9	4668	1315	40.6	---
	Permeate	11.7	4.9	108	442	0.26	---
10	Feed		5.2	6513	1275	57.8	---
	Permeate	7.8	4.8	108	427	0.27	---
15	Feed		4.9	4829	1361	39.7	700
	Permeate	7.8	4.6	257	512	0.33	5
20	Feed		5.1	5018	1237	42.6	450
	Permeate	8.4	4.0	258	650	0.39	5
25	Feed		5.0	5055	1100	36.0	400
	Permeate	9.6	4.2	195	378	0.22	5
30	Feed		5.8	5190	1211	44.9	650
	Permeate	9.7	4.0	237	347	0.32	5
35	Feed		4.8	4960	1195	38.0	700
	Permeate	8.8	4.2	200	425	0.33	5
40	Feed		4.8	5635	1420	38.0	530
	Permeate	8.4	4.3	178	551	0.40	5
45	Feed		4.6	5480	1530	42.0	500
	Permeate	7.6	4.5	164	142	0.48	5
50	Feed		4.8	5615	1488	41.3	480
	Permeate	7.6	4.4	179	305	0.42	5
55	Feed		5.4	5332	1401	35.0	380
	Permeate	8.0	4.4	211	418	0.35	5
60	Feed		5.2	5620	1282	40.9	321
	Permeate	7.4	5.0	240	359	0.38	5

[a] A measure of the lignin content.

At the start of the trial the flux rates were on the order of 16 gallons per square foot per day (gfd) at 600 psig. The flux rapidly decreased to 11 gfd and then held at this level for 35 days.

After 35 days there was evidence that heavy slime formation in the feed reservoir and in the modules was affecting the performance of the system. The liquor in the reservoir, which was on a twice weekly change schedule, was odoriferous within eight hours after makeup, and there were long stringlike slime formations floating in the fluid. Periodically, pads of slime sloughing off the tubes would block the regulating valve and the pressure would become erratic.

The flux rate decline, due to slime formations on the membranes, could be stopped and the rate restored to 8-9 gfd by ball-flushing the modules periodically with a 3/4-inch soft polyurethane ball (a procedure fully described in Section V). Later the addition of a biocide (an alkyl dimethylbenzyl ammonium chloride product) to the feed stream helped to reduce the rate of slime formation and the frequency of ball-flushing cleaning.

This carefully controlled life test run started with ten modules and was continued around-the-clock and seven days a week, with replacement of modules as they failed over a period of 14 months (433 days).

Two of the original modules, Nos. 3-19 (6552 hours) and 3-27 (6680 hours) continued in active service for nine months (Table 94). One ran to failure without replacement, (also at 9 months) three were replaced once, at shorter intervals and the others on several occasions. Eight modules remained in operating condition at the end of the run, and at that time had as a group demonstrated an average life of 4812 (200 days), or nearly seven months with the oldest at 5808 hours (242 days) and the newest at 3329 hours (139 days). Overall, the 25 modules entering upon the entire 14 months' test had averaged more than six months' operating life. Seven of these remaining 7-tube modules entered a subsequent comparative test with 18-tube modules, and their average life was extended by another month (578 hours) (see Table 96). Two more individual modules reached the 9-month life level, No. 3-68 (6684 hours) and No. 3-70 (6215 hours).

Elsewhere, the Bureau of Reclamation, U.S. Department of Interior, was reported to have had a similar bank of these same 7-tube modules in continuous service for a period of 18 months in a study conducted for the Office of Saline Water.

These results were concluded to be promising evidence that, with continuing improvement in manufacture and design, the life of tubular modules could be expected to eventually extend beyond a minimum one-year practical life and on toward a 2-year objective. The larger-scale demonstrations were undertaken with tubular design equipment on this premise and on the basis of comparative freedom from serious plugging problems experienced with capillary fiber and sheet membrane designs.

TABLE 94

MODULE REPLACEMENT SCHEDULE FOR THE SEVEN-TUBE LIFE STUDY

While Processing a 1 Percent Solids and Sulfite Wash Water

#3-19	#3-20	#3-21	#3-22	#3-23	#3-24	#3-25	#3-26	#3-27	#3-28
Out on 3-2-67 for cleaning 1813 hr	Failed 6-17-67 4128 hr	Failed 4-19-67 2942 hr	Out as mate to #3-21 on 4-19-67 2942 hr Failed 6-28-67 3720 hr	Failed 6-22-67 4244 hr	Failed 12-12-66 96 hr	Failed 5-11-67 3311 hr	Out as mate to #3-25 5-11-67 3311 hr	Failed 10-2-67 6680 hr	Failed 8-16-67 5558 hr
#3-31 In on 3-2-67 1/2 day	#3-60 In on 6-17-67 5753 hr[a]	#3-32 In on 5-8-67 Failed 5-20-67 288 hr	#3-75 In on 6-28-67 Out as mate to #3-19 2288 hr	#3-68 In on 6-22-67 5637 hr[a]	#3-18 In on 12-12-66 Out for cleaning 3-2-67 damaged 1818 hr	#4-17 In on 5-11-67 Out as mate to #3-26 5-11-67	#3-26 In on 5-15-67 Failed 5-21-67 3540 hr		#3-71 In on 8-16-67 4323 hr[a]
#3-19 In on 3-2-67 Failed 9-27-67 6552 hr		#3-34 In on 5-20-67 Failed 12-5-67 2036 hr			#3-30 In on 3-2-67 Failed 8-20-67 3840 hr	#3-33 In on 5-15-67 Failed 6-5-67 418 hr	#5-10 In on 5-22-67 Replaced no fail 6-5-67		
#3-73 In on 9-27-67 3329 hr[a]		#3-75 In on 12-5-67 3972 hr[a]			#3-72 In on 8-21-67 4221 hr	#3-43 In on 6-15-67 Failed 6-30-67 311 hr	#3-42 In on 6-15-67 5808 hr[a]		
						#3-69 In on 6-30-67 5452 hr[a]			

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[a] In use at end of run.

A field trial was set up on a calcium-base acid sulfite pulp wash water with 24 of the 7-tube modules which continued for a 23-week period. Two module failures were encountered during this period. Both modules had been used extensively before this test and both failed due to tube rupture after 1450 and 1550 hours.

A problem of much concern in the use of later designs of tubular modules with replaceable tubes was not apparent in these first life studies with the 7-tube cast-in-head modules. The rigid casting of the tubes in resin heads was an effective method of eliminating problems of sealing the connections for tubes in the end cap structures. Leakages in the end caps were a comparatively minor problem of proper gasket installation and maintenance of external module manifolding connections.

However, the structural failure of a single tube in the 7-tube module with a rigid cast-in-place head structure resulted in total failure and forced discarding of the entire 7-tube module. This manufacturer, in common with other suppliers, was researching and designing new and improved modules. Various systems were under development for replacing individual tubes or relining rigid modular structures.

One of the tubular type equipment suppliers came forth at this time (1967-1968) with new 18-tube modules having a compact head structure based upon replaceable tubes for the combined purpose of:

1. Increasing the ratio of membrane surface area to a unit of module volume.

2. Reducing the pressure drop in the tube connecting, turnaround structure of the end cap and of the manifolding connections between modules.

3. Reducing initial capital costs and the major operating charges for module replacement and maintenance.

Similar design changes were apparent in new equipment becoming available from other manufacturers.

18-Tube Modules

Upon completion of the 14-month life study with 7-tube modules, a second trial was started in February, 1968, which was initially equipped for comparative purposes, with a series of eight of the 7-tube modules remaining from the first study, in parallel with two banks of the new Havens 18-tube modules each with 3 modules in series. This arrangement provided a three bank system in which the 7-tube and the 18-tube modules could be compared while processing the same dilute calcium-base feed liquor under the same conditions of operation.

Pumping equipment was improved by converting from the rotary pumps (4 piston) to heavier reciprocating single piston pumps with variable stroke length more suitable for continuous research service. Standard bladder-type accumulators were also employed from this point on to dampen the pressure pulsations of the piston pumps at 600 psig.

The initial product water flux rates of the 18-tube modules were found to be almost 50 percent higher than for the 7-tube modules (Table 95). Quality of the product water was comparably high for both types of equipment. This indicated an improvement in the modules, and did in fact indicate an improvement in membrane performance. However, there was a serious increase in the number of module failures. Leakages in the 18-tube module end cap seal structures became a critical problem to contend with.

With six 18-tube and eight 7-tube modules on line we experienced 20 and 6 failures, respectively, during a 54-day test period.

This rapid module replacement resulted in widely scattered flux and water quality data. Observation of poor rejection was usually soon followed by module failure. The 7-tube modules failed due to tube ruptures and most of the failures in the 18-tube units were due to leaks in the seals between the individual tubes at the end cap of the module. While these leaks could be repaired on site, it was not an economically satisfactory situation in terms of time and expense for repair and replacement. All experiments with the 7-tube modules were terminated at this time when manufacture ceased.

A second trial with new 18-tube modules having components redesigned to reduce the cold flow in some of the plastic parts was inaugurated April 15, 1968. Three parallel banks of three 18-tube modules in series was set up for this test.

In this study at 600 psig, the flux could be maintained at 8 to 14 gfd (corrected to 40°C) for a recycle feed actually operating in the range of 30-35°C. A combination of pressure pulsing and ball flushing of the modules was employed during the run to develop the data shown in Table 96. Although only the optical density rejections are summarized in this table, other rejections were on the order of 96-98 percent for solids, 88-95 percent for COD, and 99+ percent for color when processing with intact modules. Losses in product water quality were traced to "module failures" due to either tube rupture or leaks at the intertube seals at the end caps.

While the first study with the 18-tube modules was plagued with leaks, this type of module failure was somewhat reduced in modules of later design. However, the number of tube ruptures markedly increased.

Between the start of the trial on April 15, 1968 and August 1, 1968 (109th day), one module failed due to tube rupture and twelve leaked heavily at the tube ends. A second tube ruptured on August 1, 1968 and by the end of the run on January 3, 1969 (266 days) twenty-eight

TABLE 95

FLUX RATES AND MODULE REPLACEMENT FOR SEVEN- AND EIGHTEEN-TUBE MODULES ON LIFE STUDY

Processing 1 Percent Acid Sulfite Wash Water

	Flux Rate, gfd at 25°C			Module Replacement, total hours at time of failure		
Week	7-Tube[a]	18-Tube[b]	18-Tube[c]	7-Tube[a]	18-Tube[b]	18-Tube[c]
0	14.5	25.2	17.5		95 46 30 24 16	95
1	9.7	17.8	16.1			318 16 2
2	7.1	10.7	10.9	5915 6215	438	438 96
3	7.4	15.2	11.0	4500 4729 4994		
4	6.2	11.3	8.9			
5	6.2	9.6	7.4	6684	899 6	966 805 1 1
6	5.6	9.4	9.7		148 24	
7	5.4	8.0	Out of system			
8	5.7	10.7	Out of system			

[a] Bank of eight modules in series.

[b] Bank of three modules in series.

[c] Bank of three modules in series.

modules had failed due to tube rupture and twenty-two by developing leaks (Table 96).

Examination of several of the tubes in consultation with representatives of the manufacturer led to the conclusion that some of the tubes had failed due to a malfunction of the tube winding machine during manufacture of these modules, as evidenced by the insufficient bonding between the fiberglass and the resin binder.

Since several of the tubes that had failures had been in modules which had been repaired several times as "leakers," there was also the possibility that the tubes had been damaged during these repair operations. To repair the 18-tube modules it was necessary to remove the tube bundle from the tight fitting product water jacket. Such a step subjected the outer tubes of the bundle to considerable friction (abrasion) and strain, as well as the possibility of wall damage from resting against or striking a sharp object while unprotected by the module casing.

Approximately 80 percent of the tube failures were observed to occur in the outer tubes around the perimeter of the 18-tube bundle within a module.

Pilot-Scale Trials with Small 1000-5000 Gallon per Day Pilot Units at Mill Sites

An on-site field trial with a neutral sulfite semichemical wash water with nine of the 18-tube modules was operated at a maximum of 550 psig. When the operating pressure was raised above this level, leaks appeared and disappeared, with resultant changes in product water quality without known correlation to operating conditions other than the pressure.

Each of the five field demonstrations for this project were preceded with preliminary runs with smaller 1000-5000 gallon per day pilot units over periods of three months or more to establish preliminary parameters of operating on each new substrate and to obtain data for design installation and operation of the larger field units. These preliminary runs provided some additional information on life history of modules. In some cases the modules were used on several different mill wastes during their test life.

Most of the small field trial experiences paralleled the laboratory module life studies for the spiral wrapped tubular designs discussed in the first part of this section. However, many variables were under study and life data were difficult to tabulate.

These initial tests of the newly developed 18-tube design constructed with replaceable tubes demonstrated much need for further improvement in details of module design and need for close control of quality during manufacture. Evidence for such improvement was apparent in successive shipments from the factory but much further improvement was critically needed.

TABLE 96

FLUX RATES AND MODULE REPLACEMENT FOR EIGHTEEN-TUBE SPIRAL WOUND MODULES ON LIFE STUDY

Processing 1 Percent Solids Acid Sulfite Wash Water at 600 psig

Weeks	Flux Rates, gfd @ 40°C			Optical Density Rejection, percent			Total Operating Hours Prior to Failure[a]					
	Bank A	Bank B	Bank C	Bank A	Bank B	Bank C	Bank A		Bank B		Bank C	
1-5	8.8	9.0	9.2	98	97	97	190 1178		132 712 1027	182 201R 1023		
5-10	8.0	8.0	8.2	98	99	95	66				1406 1386	1104
10-15	17.0	11.6	15.0	99+	99	98					113 1480R	1574R
15-20	11.2	10.7	11.4	99	99	99			2126R		3111R	
20-25	10.6	10.5	11.7	99	98	98	2520R 24R	48 333R	3167R 896R 24R 269	3040 362R 2R 1R	315R 60R 525	
25-30	9.4	13.2	13.1	96	99	99	3422R	3587R	1155R 39R 2	233R 145R		
30-35	14.1	11.6	9.4	97	77	99	177R		454	414	1689R	
35-End	13.4	15.4	13.7	99	99	99	1798		673R 100	144R	2586R	12R

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[a] R = modules with ruptured tubes, other values "leakers."

Note: Banks A, B, and C = Three parallel rows of three modules in series.

SMALL-SCALE LAB AND PILOT EVALUATIONS OF OTHER TUBULAR DESIGNS

14-Tube Modules

One of the early modules of the replaceable membrane type, produced by another supplier consisted of 14 polyester reinforced braided fiberglass tubes 4 feet long and one-half inch inside diameter. A strip of cellulose acetate membrane was inserted as a lining to form a tube with a loose seam resting against the woven fiberglass wall. A slight overlap of the lengthwise edges of the cellulose acetate strip provided a compaction seal under operating pressures above about 100 psig. This module was also equipped with turbulence promoters inside of the tubes to permit lower operating velocities without concentration polarization.

Operation of this module at velocities one-fourth those for an open one-half inch tube permitted the installation of more modules (tubes) in parallel for a pump of given flow rate output. Recycle to reach a given concentration level could be reduced. These appeared as substantial advantages of this design.

Our early trials with one of these modules 1, 5, 10, and 20 percent solids concentration of calcium acid sulfite wash water were conducted at 400, 600, and 800 psig.

Excellent flux rates, even at 20 percent solids, could be achieved at 800 psig (Table 97) and at flows as low as 0.25-0.5 gpm (12-25 cm/sec velocity in empty tubes). At the same time rejections on the order of 96-98 percent solids, 93-98 percent COD, and 98-99 percent optical density were possible under these operating conditions (Table 98).

Shortly after this preliminary trial was completed, however, the module failed with massive leakage, apparently due to the opening of one or more of the membrane-overlap seams during the time the module was at atmospheric pressure. The support tube did not rupture.

In July 1969 a second module was received, along with notification that a slight positive pressure should be maintained at all times on the high pressure (liquor) side of the tubes.

This five foot module was placed on life study with the 1 percent solids calcium-base acid sulfite liquor. The module produced colored product water samples occasionally. The color indicated continuing problems with leaks at the seam of the membrane. The flux rate gradually declined (Table 99). After 330 hours (2 weeks) of operation, the flux rate had declined from an initial 24 gfd to 13 gfd (a 40 percent loss) and there was evidence of membrane (or module) fouling.

At this time a motorized bypass ball valve with less rapid action was installed in the pressure line between the pump and the module to permit slower and less violent reduction of the pressure from 600 psig to 25 psig for two minutes every four hours (pressure pulsing). During the

TABLE 97

FLUX RATES WITH BRAIDED FIBERGLASS TUBULAR MODULES

Tap Water And Ca-Base Wash Water

Feed Solution	Inlet Pressure, psig	Temperature, °C	Average Linear Velocity, cm/sec	Flux Rate, gfd
Tap water	600	34.5	48	19.7
	800	34.5	46	24.1
1 Percent solids wash water	800	33	29	18.8
	800	34	16	18.3
	800	33	6	16.6
	600	35	30	13.1
	400	34.5	21	9.9
5 Percent solids wash water	800	35	30	14.4
	800	34	16	13.9
	800	33.5	7	12.3
	600	34	31	11.0
	400	33	32	6.8
10 Percent solids wash water	800	34	31	11.4
	800	34	17	10.3
	800	34	7	9.0
	600	34	31	8.0
	400	34	32	6.9
20 Percent solids wash water	800	34.5	31	9.9
	400	34.5	32	4.6
	800	36	65	9.7

TABLE 98

PERMEATE QUALITY FROM BRAIDED FIBERGLASS TUBULAR MODULES

Ca-Base Wash Water at Various Concentration Levels

Feed Concentrations

Solids Concentration, percent	Solids, mg/l	COD, mg/l	Calcium, mg/l	Optical Density at 281 nm
1	11300	14700	550	86.6
5	55200	37200	2500	450
10	81400	111900	2700	640
20	-----	281000	7500	1450

Rejection Ratios, percent

Solids Concentration, percent	Solids, mg/l	COD, mg/l	Calcium, mg/l	Optical Density, at 281 nm
1	98	98	97	99
5	98	97	98	99
10	96	95	--	98
20	--	93	92	98

next 170 hours (7 days) by this modified method of operation, the flux rate remained relatively constant or increased slightly, but the quality of the product water continued to deteriorate below acceptable standards and the study was discontinued.

For other tubular designs, pressure pulsing seemed to be one of the better methods of reducing severe fouling in the processing of pulping effluent containing suspended solids and colloidal suspensoids. The unsealed membrane seams of this modular design were indicated to be impractical for operating by that method. The manufacturer then supplied two newly redesigned braided fiberglass modules, complete with "seamless" cellulose acetate membrane-tube replacements. These were put on line for an extended module life study on March 24, 1970. A third module of the same design was added on June 22 after the unit had been in operation (2070 hours, 88th day). Pressure pulsing (600 psig to 24 psig) was practiced on an 80-second per hour cycle throughout this run.

The physical stability of these vertically mounted modules, the flux rates, and the product water quality (Table 100) were excellent for approximately 5800 hours (35 weeks). Occasionally color appeared

TABLE 99

FLUX RATES AND PERMEATE QUALITY WITH FOURTEEN-TUBE MODULES ON LIFE STUDY

Processing 1 Percent Solids Acid Sulfite Wash Water

Hours	Flux Rate, gfd at 40°C	Optical Density of Permeate, 281 nm
1	24.5	0.54
48	19.9	4.4
167	15.4	2.1
209	15.8	2.7
237	19.8	2.8
330	13.0	2.1
379	12.0	3.3
425	11.5	5.8
502	16.1	35.0

in the permeate water for short periods of a day or so in samples from Module 1, but at no time did the rejections fall below 90 percent for solids, 85 percent for BOD_5, 90 percent for COD, and 90 percent for optical density (color). In most product water samples taken weekly, these rejections were on the order of 98 percent, 97 percent, 98 percent, and 99 percent, respectively.

During the first 30 days of operation, the flux rates declined from a starting value of 11.2-12.5 gfd to levels of 6-7 gfd for the two modules first placed in operation. Within 20 days after the third module with a tighter membrane had been installed, its flux rate had also levelled off at 7 gfd from an initial 9 gfd.

After approximately a month of operation we noted a buildup of a gray-black "furry" slime coating on the outside of the individual tube of Modules 1 and 2. Washing the outsides of the modules with tap water and an air-water mixture did little to remove the deposit, but periodic washing with an enzymatic laundry detergent followed by a rinse with pH 3 water did keep the formation from spreading or developing into layers, which would slough off into the product water. Several trials with one-half hour soakings of the entire outside of the module in 100 ppm copper sulfate had little effect.

TABLE 100

FLUX AND PERMEATE QUALITY WITH FOURTEEN-TUBE MODULES ON LIFE STUDY

Processing 1 Percent Solids Acid Sulfite Wash Water
(600 psig Operating Pressure)

Week	Stream	Flux Rate, gfd at 40°C	Solids,		BOD$_5$,		COD,		Optical Density,	
			mg/l	Rejection, percent	mg/l	Rejection, percent	mg/l	Rejection, percent	at 281 nm	Rejection, percent
1	Feed		9820	--	2270	--	12020	--	73.2	--
	P-1	9.9	398	96	154	93	520	96	3.1	96
	P-2	9.4	98	99	66	97	133	99	0.68	99
5	Feed		9692	--	2543	--	12320	--	71.8	--
	P-1	8.7	111	99	77	97	114	99	0.54	99
	P-2	8.2	112	99	93	96	117	99	0.48	99
10	Feed		11544	--	3185	--	14460	--	86.2	--
	P-1	8.5	134	99	93	97	168	99	0.77	99
	P-2	7.9	106	99	84	97	135	99	0.66	99
15	Feed		11026	--	5110	--	13460	--	81.1	--
	P-1	8.6	267	98	136	96	321	98	1.58	98
	P-2	8.2	124	99	78	98	103	99	0.51	99
	P-3	7.7	119	99	82	97	112	99	0.54	99
20	Feed		10670	--	3465	--	13330	--	82.1	--
	P-1	9.4	678	94	492	86	914	93	4.98	94
	P-2	7.4	135	99	171	95	207	98	0.75	99
	P-3	6.7	146	99	152	96	226	98	0.84	99
25	Feed		11244	--	2690	--	13900	--	85.0	--
	P-1	8.2	690	94	229	92	879	94	5.23	94
	P-2	7.2	227	98	62	98	119	99	0.63	99
	P-3	6.7	454	96	154	94	578	96	3.55	96
30	Feed		10882	--	2630	--	13820	--	80.8	--
	P-1	11.9	1091	90	246	91	1386	90	7.78	90
	P-2	6.5	136	99	42	98	133	99	0.63	99
	P-3	7.4	502	95	115	96	618	96	3.50	96
35	Feed		11296	--	2280	--	13460	--	85.6	--
	P-1	9.9	310	97	92	96	326	98	1.62	98
	P-2	5.1	139	99	38	98	112	99	0.58	99
	P-3	7.5	197	98	58	97	206	98	1.22	99
40	Feed		11228	--	2750	--	13740	--	81.2	--
	P-2	3.8	1122	90	340	88	1359	90	7.78	90

The third module, which was washed with the detergent solution from the start of its inclusion in the series, did not develop the slime coating and the tubes remained clean.

Problems arising from extended operation of these 14-tube modules were mainly concerned with fouling problems which were difficult to control at low velocities. Some leakage was apparent but rupture of the support structure was experienced on only one occasion.

16-Tube Woven Fiberglass Modules

This modular design incorporated the idea of a replaceable tube mounted on heavy stainless steel end plates fabricated with tubular U bend interconnections. These modules were vertically mounted and the product water drained down the tube walls into collecting pans.

The cellulose acetate membranes were cast inside of the woven fiberglass tube which had an O-ring coupling on each end for attachment to the end plates. This O-ring coupling was excellent, with trouble-free, fast action during replacement and this design appeared in other ways advantageous in terms of mechanical design features as compared with other tubular systems. The top end plate was mounted rigidly and the bottom allowed to float free; thereby providing a slight tensile stress on the tubes, eliminating the compressive stress which apparently had caused difficulties in some of the other tubular designs.

The first two of these modules contained 16 tubes in a modular configuration, 4 x 16 inches (end plate size) by 106 inches long. The tubes were 9/16 inches inside diameter and contained 1.2 square foot of membrane per tube.

Data in Table 101 summarizes test results in terms of flux rate (gfd), product water quality (percent rejection) and tube failures. The flux rates and product water quality were both excellent, but the tube failures, six in a period of eight days of operation (average tube life of 140 hours), caused discontinuation of the study. Of the six failed tubes, three had pinholes in the tube walls and three tore loose at the tube coupling joint.

The second generation of tubes arrived in our laboratories in April 1970 and were mounted on the module end plates used in the first trial. The end plates were modified with tie rods between the end plates in an attempt to relieve tension on the tubes without causing the tubes to be under compression.

Within a few hours tube failures were apparent, which were similar to those in the first study; namely, ferrule separation at the tube ends. The slightly unmatched lengths of the tubes under different pressures resulted in the tubes "bowing and whipping" with each stroke of the pump. Eventually this seemed to result in fatigue rupture of the tube, at the rigid joint with the tube ferrule.

TABLE 101

FLUX RATES AND MODULE REPLACEMENT FOR SIXTEEN-TUBE BRAIDED MODULES ON LIFE STUDY

Processing 1 Percent Solids Acid Sulfite Wash Water at 600 psig

	Flux rate, gfd at $40^{\circ}C$		Optical Density Rejection, percent		Operating Hours Prior to Tube Failure	
Hours	Module A	Module B	Module A	Module B	Module A	Module B
			First Trial			
45	11.1	10.9	99	99		
139	12.4	9.9	99	99	126,130,138 158,158	134
			Second Trial			
4	24.2	22.6	98	98	----	4
117	17.5	16.8	93	96	----	----
253	14.2	9.1	99	99	266,260,253	205,267,267 267

Flux rates varied widely during this test period, from 26 to 7 gfd depending upon the age of the tubes in the module. The quality of the permeate was quite high (Table 101), even at the higher flux rates of 18-22 gallons per square foot per day.

Within a 16-day period, ten tube failures were experienced and the study was again discontinued due to lack of tube replacements. Structural failure of the membrane support tubes was a major problem in testing this type of tubular equipment.

36-Tube Modules with Nonporous Tubes

During the latter part of December 1969, two 36-tube modules were received from still another manufacturer for evaluation in the life study program. These modules were arranged with six banks of six tubes, each in a 4 x 11 x 106 inch space. The inner tube connections were an integral part of the end plates and provided for series flow through all 36 tubes. Optional end plates of a different design could also be used to provide parallel flow through the 36 tubes for use in modified methods of processing at high flow rates.

The membranes were cast on porous paper support tubes and could be replaced by removing the end plates from either end of the module.

Data on flux rates and product water quality for the two modules are given in Table 102. Data are also presented from operation of a third module which was received on January 17, 1970 near the end of the run. While the product water quality was generally excellent, there were periods of highly colored permeates immediately after pressure-pulsing cycles, and the modules failed by massive leakage after 611, 822, and 276 hours (Modules 1, 2, and 3, respectively).

Shortly after the trials with these three modules were discontinued, a company representative attempted to modify all three by installing newly designed end plate gaskets and new tubes. Difficulties were experienced in removing the inner membrane tubes, and the modules were returned to the factory where special tools were available for removing the tubes without damage to the inner support structure. Swelling of the replaceable paper tubes may have been related to the pressure pulsing system with back flows, for which the modules had not been designed. However, the swelling of the paper tubes did not appear to be the cause of tube failures. Cracks were apparent in the plastic sleeves at the tube ends where they mated with the O-rings of the end plates.

Three newly redesigned modules were installed on February 11, 1970 for series operation through the three in series. Due to the difficulty encountered in the first trial, care was taken to provide atmospheric discharge of both the product water and the concentrate to avoid siphoning and back flow problems which may have contributed to the tube swelling and seizure.

TABLE 102

FLUX RATES AND REJECTIONS FOR THIRTY-SIX TUBE MODULES ON LIFE STUDY

1 Percent Acid Sulfite Wash Water at 600 psig

Hours	Stream	Flux, gfd at 40°C	Rejection, percent			
			Solids	BOD_5	COD	Optical Density at 281 nm
1	P-1	14.2	--	--	99	99
	P-2	15.0	--	--	99	99
88	P-1	11.5	99	97	99	99
	P-2	11.8	99	97	99	99
257	P-1	9.0	99	94	98	99
	P-2	10.5	99	94	98	99
425	P-1	8.1	99	94	98	99
	P-2	10.6	99	96	99	99
567	P-1	6.8	99	96	99	99+
	P-2	9.6	99	96	99	99+
728	P-2	9.6	99	98	99	99
45	P-3	13.2	99	98	99+	99
214	P-3	11.4	99	98	99	99

The flux rates steadily declined in spite of pressure pulsing (30 seconds per hour); weekly treatment with a 1000 ppm copper sulfate solution; and an increase in fluid velocity from 3.4, 3.0, and 2.8 feet per second in the three modules to 4.1, 3.8, and 3.5 feet per second, respectively.

Product water quality remained high during the first part of the study. But by the end of the twelfth week (1946 hours) all were producing colored permeates, although only Module 3's rejections were markedly low.

Since the manufacturer had developed new seal rings, the modules were rebuilt with all new seal rings and six new tubes in Module 2 and two in Module 3. The difficulty was encountered in removing the tubes in this last replacement, in spite of the fact that back flow and siphoning had been eliminated.

The third trial terminated after seven days (160 hours) due to the reproduction of colored permeates in all modules of the line. All three were returned to the manufacturer for refitting.

The three completely new modules in the fourth trial developed colored permeates in Modules 1 and 2 after 275 hours and 280 hours, respectively, with gradually decreasing quality until both were removed from the system at the 851st hour. On the other hand, Module 3 produced high quality permeates until the 1118th hour, when the permeate suddenly colored and the trial was discontinued.

The series of tests with the 36 tube modules, with replaceable membranes mounted in paper tubes, showed evidence of leakage of the sleeve sealing connections within the membrane support structure, but no evidence of failure of the membrane support structure. These modules provided much evidence of highly developed engineering design of the support structure and of the excellent manifolding system. The leakage problem within the membrane support structure was being intensively studied and advances were indicated at the time of terminating the tests.

Life Performance in Large-Scale Field Trials with the Trailer-Mounted Unit

The advancing technology and growing experience with large laboratory and small pilot RO units having membrane areas in the 10 to 100 sq ft category provided the base for designing the larger trailer-mounted unit which could more adequately evaluate the practical problems and economics of field-scale commercial operation. Actual experience with the life performance of a large RO system was therefore an important objective in planning the experimental program for the field test unit designed and constructed in 1968. This unit as delivered in October 1968 had 387 modules with 6580 sq ft of working membrane area, plus 20 spare modules for replacement. Special planning included setting up a card catalog for following the individual life history of all modules on this unit.

A first test of performance capabilities of the membrane system, in terms of resistance to damage during shipment for long distances, occurred in transporting the trailer unit complete with modules mounted in place some 2400 miles from the factory in San Diego to the site of the first demonstration at the sulfite pulp mill in Appleton, Wisconsin. The five banks of modules were mounted on adjustable channel steel racks with flexible metal hose connections to the multi-valved manifolding system at the completion of the factory testing program prior to delivery. Only a minimum of taping and support blocking was felt to be required, and this appeared to have been fairly adequate, although a few modules did shift substantially out of line without apparent damage in transit. All but a few of the topmost modules high in the stacks were still filled with water on arrival after 5 days enroute.

The operation and performance of the trailer-mounted unit in the three field demonstrations have been reviewed in detail in Section VII of this report. The reader should refer especially to the analysis of downtime reported in Tables 32, 37, and 47 for each of the demonstrations. The following paragraphs summarize the life expectancy performance of the 387 modules originally supplied with the unit in October 1968, and also of the performance of 238 modules which had been returned to the factory for rebuilding in the period of field demonstration No. 3.

Table 103 summarizes the accumulated data.

TABLE 103

LIFE PERFORMANCE OF 387 MODULES ON TRAILER-MOUNTED FIELD UNIT

	Field Demonstration No. 1	Field Demonstration No. 2	Field Demonstration No. 3	
			1st Period	2nd Period
No. modules in service	387	387	387	238[b]
Hours available on-site operation	1386	985	841	226
Total trailer operating hours	690	594	466	211
No. modules failed and replaced	8	46[a]	62	58
Type of module failure				
Loss of membrane	0	6	0	0
Tube rupture	6	30	55	14
Leak in tube seals	1	2	4	44
$CaSO_4$ scale	1	8	3	0
Failure rate per 100 operating hours per 1000 sq ft of membrane	0.176	1.178	1.996	6.794

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[a] 44 Modules partially plugged with loose membrane (from other modules) were cleaned and returned to service.

[b] 238 Modules rebuilt at factory.

The three 3-month trials extended over a period of nearly 12 months. Records show a total of 3438 hours were available for operation at the three field sites, of which 1967 hours, or about one-fourth of the one-year period resulted in actual operation of the unit under pressure with mill effluent feed. During the first field demonstration, 8 module failures occurred during 690 hours of operation. Since the manifolding system was equipped with shut-off valves on each set of from 3 to 5 modules, the group of modules in which a failure had occurred could be closed out of the system without need for shutting down the whole unit. Repairs or replacement could be conducted when time permitted during the course of sustained operation, and no shutdown time was experienced in this run because of module failures.

In the second demonstration, available operating time totalled 594 hours, but in this case 46 modules failed or were replaced during the run. An additional 44 modules were found to have partial or complete plugging with loose membrane. Nine and one-half hours of operation time were lost when it was found necessary to shut the entire unit down to locate, to backwash, and to replace those 44 modules. Apparently, a rare case of membrane stripping occurred, and the loose membrane traveled through the remaining affected modules downstream. Most of the modules were found to be easily back washed to remove the loose membrane. Those were cleaned, tested, and returned to service. Examination showed a total of 6 modules from which the membrane had been stripped in one or more tubes, but it could not be determined whether more than one module of the six was the original cause of membrane loss since the loose membrane from one module could be cause for stripping or plugging in modules downstream.

A much more serious effect on life expectancy of the total number of modules arose from the 30 modules having structural failures of the membrane support system, with resultant rupture during the course of this second demonstration.

In the third demonstration, 62 module failures and replacements occurred during the first period of 466 operating hours. Fifty-five of these failures were due to tube rupture, 4 to apparent leaks in tube seals, and 3 were found to have calcium sulfate scale. Module failures accounted for 23 hours of downtime.

After rebuilding 238 of the modules at the factory, another 211 hours of operation occurred in the second period for this third field demonstration. Module failures and replacements totalled 58 and were cause for 23 hours of downtime. Of these failures, 14 were due to tube rupture. In the second period most of the failures were due to 44 tube seal leaks, but no downtime resulted from that problem. It was apparent that the small plastic tube seal inserts used during the rebuilding program at the factory were faulty, since leakage had been a minor problem theretofore.

An attempt was made to evaluate the rate of module failure in terms of downtime for each hundred operating hours per thousand square feet of membrane. For the first demonstration, this downtime factor was calculated to be 0.176. In the second demonstration it rose to 1.178, while the first half of the third field demonstration showed 1.996 and the second period 6.794. This evaluation factor, based on failure of module units, does not include allowance for variation in size and cost of the wide variety of modules being developed and marketed. The module is the failure unit under consideration. It will be of interest to follow development and use of this or a similar factor for comparative evaluation of failure as cost evaluation of membrane systems develops.

The rate of module failures at 0.176 during the first 3-month demonstration appeared promising of becoming a supportable item of operating cost in a large installation. The failures occurring later in the life of the module support structure during the second 3-month field demonstration were found to be far too high. The rupture failures at the 2.0 factor level which occurred as aging advanced in the first period of operation during the third demonstration confirmed the rising rate of failure at levels far beyond economic feasibility. Continued operation of the trailer unit could not be justified until more reliable membrane modules could be proven out.

Membrane life expectancy tests were subsequently continued with equipment supplied by a number of principal supply firms introducing new and improved equipment during the period 1968 through 1971.

Discussion of Life Expectancy of RO Equipment

The overall picture for life performance of membrane equipment of these studies was disappointing because the critically high costs of membrane module maintenance and replacement substantially reduced commercial feasibility of the RO concentrating process at the stage of RO engineering and development prevailing during the 3-1/2 to 4 years of study on this research and demonstration project.

High levels of technical performance for the RO process in terms of capabilities for concentrating dissolved substances from dilute solution has appeared excellent throughout this project. But commercial feasibility for large-scale operations plainly must wait for proven success in accomplishing the next step in design and production of membrane equipment. A much higher level of reliability for sustained operation at life expectancy levels greater than 12 months must be attained.

The capillary fiber and the spiral wound sheet membrane systems showed good evidence of having structural stability and freedom from internal leakages, but the experience gained during the course of this 3-1/2 year demonstration showed few of the industry effluents which were subject for study to be free of problems of fouling of the membrane or alternately plugging of the passageways in these types of membrane equipment.

On the other hand, tubular-type module configurations were found capable of handling the fouling problem at high velocities. Failures due to plugging of the large passageways, 1/2 inch in diameter or greater seldom occurred. But the provision of structural stability and freedom from serious leakages for the tubular system has been an engineering design problem not completely solved and proven during the period of this research and demonstration grant study.

Several causes might have been responsible for structural failure in the tubular membrane equipment. Support structures based upon high strength, corrosion-resistant material such as 316 stainless steel or with other types of less expensive metal structures, protected by coatings or resin linings, were proven quite adequate in eliminating tubular rupture. But these materials of construction had to bear a serious cost handicap, and all manufacturers producing prototype equipment with expensive metal support structures or housing were indicated to be advancing design of commercial equipment toward use of lighter weight, less expensive composite structures, such as resin-bonded fiberglass and the like.

The results of the studies reported for this project strongly indicate that the resin-bonded fiberglass structures available for these studies were subject to stress fatigue in sustained operation after a period of several months. The stresses of high pressure operation at 600 psig or higher were greatly accentuated by programmed pulsations and by fluctuations during the course of shutdowns and startups during six months and more of operations. Serious leakages were probably also associated with stress fatigue in the connecting seal structures in a number of types of equipment tested. Use of O-ring seals has appeared to be an excellent answer to the problem of sealing internal connections within the membrane support structure. It was plain that further improvement in design could logically follow intensive engineering studies known to be in progress.

Basically, it may be concluded that the life expectancy of RO equipment is a problem of improvement in terms of engineering design and quality control during manufacturing operations. The structural failure problem seems solved by high levels of engineering design for the capillary fiber and spiral wound systems. However, these excellent qualities are counterbalanced by the problems inherent in design of equipment which can provide high velocities and turbulence across the surface of the membrane to keep the membrane clean and free from fouling problems. The studies in this grant project have therefore trended toward preference for tubular systems because of the proven capability to maintain high levels of flux through the membrane at high rates of rejection with greater degrees of freedom from fouling or plugging problems.

Emphasis in these studies has been heavily directed toward the search for reliable designs and configurations for the membrane support structures. Membrane failures as such have been surprisingly few, and apparently are within the range of commercial feasibility at the present stage of development. Cellulose acetate membranes, if operated at moderate temperatures below 45°C, and within pH ranges of about 3.0 to 7.5, have appeared adequate in terms of life expectancy. Preliminary tests with nylon and other types of membrane formulations also appear promising in terms of membrane life expectancy if operated within recommended limits for temperature, pH, and the like, and apparently have substantial advantage over cellulose acetate in operating over a wider range of temperature and pH. The problem then appears to be a matter of improving the structural design and the quality of manufacturing operations for the membrane support structures.

Conclusions as to Life Expectancy and Sustained Performance of RO Equipment

Life expectancy of RO membrane equipment must be adequate as measured on two basic criteria:

1. RO membrane equipment must be capable of sustained operation free of problems of being plugged or of becoming irreversibly fouled by suspended particulates, colloidal suspensoids, or by large molecular weight solutes contained in the feed liquor or which develop during concentration.

   The plugging and fouling problem is of particular concern in processing industrial effluents as discharged in pulp and paper manufacturing operations based upon wood-derived organics and inorganic pulping chemicals. The extended evaluatory studies conducted under this research and demonstration grant point to the self-cleaning capabilities provided by high velocity and highly turbulent flows within tubular RO systems as being best adapted to processing such effluents. Capillary fiber and sheet membrane pack systems at their present stage of development apparently will require high levels of pretreatment for most of these industrial effluents. Such pretreatment requirements might be provided by ultrafiltration.

2. The life expectancy of RO membrane equipment must be adequately proven in terms of long-term stability of the membrane support structure, and of sustained leak-free performance of internal connections based upon the support structure. The studies under this R & D Grant project have failed to demonstrate adequate leak-free, life expectancy of membrane support structures of the tubular conformation as designed, manufactured, and available for testing within the 4-year program period.

   The requirements of establishing the feasibility of RO membrane processing systems seem best fulfilled by tubular conformations in terms of sustained performance free of plugging and fouling problems when treating dilute pulp and paper processing effluents. On the other hand, the capillary fiber and sheet membrane systems have been indicated as most advanced in terms of freedom from failure of the membrane support structure and associated leakage of internal connections.

None of these systems were found capable of meeting both of these requirements basic to establishing large-scale feasibility for processing of these dilute industrial processing effluents.

SECTION X

PROCESS ECONOMICS

Justification for the extensive application studies undertaken on this Research and Demonstration Grant Project for evaluation of reverse osmosis as a method of concentration processing of dilute pulp and paper manufacturing effluents has necessarily required frequent assessment and reassessment of economic feasibility. Process concepts were new and novel when undertaking the project in 1966. Reverse osmosis is still under intensive research and development, and is not yet in large-scale commercial practice as of January 1972. As such, it has not been possible to have the benefit of actual experience in developing capital costs for this membrane equipment in large-scale commercial production, nor can conclusions be drawn on the firm base of actual costs of operation from large-scale operations of the RO concentration process in other fields, such as saline water conversion.

Nevertheless, extended engineering studies have been reported[28,29] upon which fairly adequate estimates of the present and future economic outlook could be established. Personal interviews and letter surveys with responsible executives and engineers in the RO field have tended to confirm the estimates in the above-cited cost studies for the Office of Saline Water. These surveys have indicated capital charges might be expected to be in the range of $1.00 per installed gallon of permeate water production for plants producing one million gallons per day, and also have forecast a range of 50¢ to $1.50 per 1000 gallons for cost of the permeate water produced as a measure of operating charges. These estimated and preliminary ranging figures have been in use with qualifications for the purpose of designing, directing, and evaluating progress of developing the RO process.

However, progress of membrane equipment suppliers has been slow in achieving projected minimum levels of performance and long-term life expectancy of the modular membrane structures during the four-year period of these project studies. Although technical developments have in other ways been excellent and important, it has therefore been necessary to substantially increase those preliminary estimates in the cost evaluations for this summary report. Capital costs for equipment remain high, but of more concern are the operating charges for maintenance and replacement of short-lived RO equipment, which in some instances of pilot-scale experience have been estimated to range to 60 or even 80 percent of total operating charges at 1971 levels of performance. These high charges should be greatly reduced when large-scale production of membrane equipment is achieved. Evidence does point to substantial advances by the equipment suppliers.

The objectives for this summary of process economics are directed to evaluating the experience gained in the laboratory, pilot, and field demonstrations in terms of existing conditions. Needed areas for improving the economics for putting RO to active use in concentrating

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dilute pulping industry effluents can be better pinpointed and progress accelerated in achieving those goals.

Since membrane equipment costs will in all probability remain high for some time, we can expect the first industrial applications of RO will be on a modest scale for concentration of wastes containing marketable values, and in this manner partially balance the large expense of early stage RO process developmental charges. Larger scale, low-cost concentration processing of dilute wastes can then be expected to follow later on when membrane equipment is marketed in sufficient volume to benefit from the reduced costs of large-scale commercial production.

In order to better evaluate the costs which might be applicable to conditions prevailing at the five sites of the individual field demonstrations conducted for this project, a computer program was developed which could provide a comparable picture based on the actual waste flow processed, and upon operating conditions, power costs, and other significant variables. No attempt was made to conduct a detailed engineering cost survey, and the data presented in Table 104 should be so understood and evaluated as a preliminary study appropriate to the present state of the art for manufacture and operation of RO equipment.

Waste flows studied at these mills ranged in volume from 125,000 gal. per day to 1,000,000 gal. per day, and the solids concentrations of the effluent to be processed varied from 1/2 percent solids to 3.0 percent solids. Two sets of cost data were compared. The first was based on good RO processing experience obtained in tests on these wastes with 1968-1970 Havens modules, and the second on high performance membranes which became available from several suppliers for field testing in 1971. Flux rates on test salt solutions with use of the older membrane equipment were at a level of 12.5 gfd, while the new membranes delivered at twice that flux rate. Several of the factors used require further definition:

> All data were based on operations at 600 psig feed pressure and 35°C.
>
> Module cost complete with membranes was quoted at July 1972 expectations of \$9.30/sq ft of effective surface.
>
> Module maintenance charges at \$24/module/year were quoted to cover cost of servicing, back washing, repairs, and labor for replacement with 2-year membrane life.
>
> Power cost varied with the mill between 0.6 and 1.2¢/Kwh.
>
> Module depreciation was based upon 5-year life of the module support structure.

TABLE 104

INDICATED CAPITAL AND OPERATING COSTS OF REVERSE OSMOSIS UNITS BASED UPON FIVE FIELD DEMONSTRATIONS — CALGON-HAVENS 18-TUBE TUBULAR MODULES

Reference Pressure = 600 psig
Reference Feed Liquor Temperature = 35°C
Module Cost = $9.30 per sq. ft. of Membrane
Module Maintenance Cost = $24 per Module per Year (2 year life of membrane)
Cost of Electric Power = 0.6-1.2¢ per Kwhr
Module Depreciation = 5-Year Life of Module Support Structure
Non-membrane Equipment Life = 5 Years
Number of Concentrating Stages = 3
Number of Modules in Series in Each Stage = 2

Feed Liquor	Design Capacity of RO Unit, thousand gpd of feed liquor	Concentration Range, g/l	Demonstration Modules[a] (Reference 5000 mg/l NaCl Flux Rate at 600 psig and 35°C = 12.5 gfd)				Latest Modules[b] (Reference 5000 mg/l NaCl Flux Rate at 600 psig and 35°C = 25 gfd)			
			Overall Average Flux Rate[c], gfd	Total Number of Modules	Total Capital Cost[d], thousand dollars	Total Operating Cost, $/1000 gal. product water	Overall Average Flux Rate, gfd	Total Number of Modules	Total Capital Cost, thousand dollars	Total Operating Cost, $/1000 gal. product water
Calcium-base acid sulfite liquor	500	12-100	9.6	2923	602.0	1.54	18.9	1485	343.0	0.95
NSSC white water	144	20-100	9.5	813	207.0	1.94	19.2	415	133.0	1.20
Ammonia-base acid sulfite liquor	125	30-100	7.9	704	179.0	2.21	15.5	358	116.0	1.48
Caustic-stage kraft bleach effluent liquor	1000	5-50	11.2	5207	1050.0	1.32	22.2	2580	582.0	0.82
Chemimechanical pulp mill water	550	6-100	11.0	3025	658.0	1.35	21.5	1544	387.0	0.83

---

[a] Used throughout the 5 demonstration sites.

[b] Recent laboratory and pilot plant experience.

[c] Overall average flux rate = $\sum_{i=1}^{n} W_i F_i \Big/ \sum_{i=1}^{n} W_i$ where n = number of concentrating stages
F_i = average value of flux rate in the i-th stage
W_i = percentage recovery of water in the i-th stage
$\sum_{i}^{n}$ = summation over n stages

The calculations of the overall average flux rate were made separately in the computer program, allow a sufficiently large number of concentrating stages.

[d] Total capital cost includes: [illegible] for each manifolding unit of 6 modules
10% spare modules for all waste flows
10% additional for pulsing of NSSC liquor
$10,000 automated instrumentation/each 0.5 mgd.

Non-membrane equipment as pumps, instruments, piping, etc., were based on a 5-year life.

The number of concentrating stages were based on a 3-stage optimum system.

Each set of modules contained two in series.

Manifolding costs were estimated at $100 per 3 sets of 2 modules in series (6 modules).

Ten percent spare modules were allowed overall, and 10 percent additional modules were provided as an allowance for downtime during periodic pulsing of the system to control fouling problems.

Instrumentation capital costs were estimated at $25,000 for each half million gallons of permeate production per day.

The computer programming of flux rates was conducted separately for each substrate.

Results of Computerized Cost Evaluation

The data on capital costs for RO installations at the five mill sites tended to confirm the earlier estimates of $1.00 per gallon of daily permeate water production on the basis of experience, with membrane equipment available and used during the course of these studies in the period 1967-1970. Substantial capital cost reductions of 10 to 40 percent were indicated for use of the new high performance membranes released by several suppliers for field testing in 1971.

The capital cost data in Table 104 would seem to indicate that mills might build plants to concentrate dilute effluents of from 100,000 gpd to one million gpd at costs in the range of $1.00 per daily gallon of permeate water production.

The critical charges for sustained operation and maintenance of an RO concentrating system were, however, much higher than predicted in the preliminary estimates, ranging from $1.32 to $2.21 per 1000 gal. of permeate flow, with membrane equipment used on this project to a range of $0.82 to $1.48 per 1000 gallons for the newly available high performance membrane equipment.

Reverse osmosis is not a complete process of waste treatment, and additional charges must be added for final disposal or utilization processing of the concentrate.

However, some perspective as to how the costs provided in Table 104 can be evaluated as part of a waste treatment system can be gained by comparison with the costs of bio-oxidation processing for conventional disposal type treatment to reduce the BOD_5 of such wastes. A rule of the thumb cost estimate for activated sludge or trickling filter treatment at 4-1/2 cents per pound of BOD_5 at the 90 percent removal basis has been quoted at times in recent cost surveys. The BOD_5 values for the five effluents listed as feed liquors in Table 104 have been provided in the various individual field study reviews in Section VII and may be summarized as follows:

	Pounds per 1000 Gallons	Biological BOD_5 Removal $/1000 Gallons at 4-1/2¢/Pound
Ca-base wash water	25.87	$1.16
NSSC white water	19.52	0.88
NH_3 wash water	62.5	2.82
Alk. ext. KBE	1.6	0.07
CM wash water	58.7	2.64

The RO charges provided in Table 104 can be interpreted as marginally competitive against proven disposal processes as long as BOD_5 removal is the principal standard of environmental quality to be complied with in treating these wastes. Bio-oxidation in aerated oxidation lagoons may accomplish satisfactory levels of BOD_5 removal at substantially less cost than by the activated sludge or trickling filter systems. Aerated lagoons, whenever feasibly installed, would be the choice for disposal treatment of these wastes. Other factors do affect the choice, however.

Although RO is not in itself a complete treatment process, its possibilities for achieving complete treatment in an integrated system are distinctly advantageous, and comprise the justification for the studies reported and for continuing research and development.

> Solutes are recovered in the concentrate at high levels of rejection for final disposal or for recovery and utilization of any values.
>
> Permeate water is of high quality for recovery and reuse in the mill system.
>
> Closure of the mill water system is the goal of complete waste treatment.
>
> Recovery of values from the concentrates and in the form of reusable permeate water can substantially reduce the cost of complete treatment.

The evaluation of RO and of the costs of such processing has been advanced in a supplementary RO project conducted by the staff of Green Bay Packaging Inc. at the site of the second field demonstration. This organization has specialized processing conditions peculiar to that mill, and goals have been established for long-range closure of their mill system. These conditions have encouraged further studies for application of RO to the concentration of their on-machine wash water or "white water" effluent.

The mill staff has conducted a substantial program of pilot-scale evaluations independent of the studies covered in this report during 1970-71. Basic results of the original project findings are being confirmed and interest continues at that mill, but adverse experience with module maintenance and replacement problems has been such that they have assigned far higher charges in this category. The previous table (104) listed the module maintenance charge at $24 per module per year. The Green Bay experience with the equipment they have tested points to $100 per year. Modified cost data based on information supplied by the mill staff are provided in Table 105.

The computer run has evaluated and proven a substantial optimization results from the design of the module manifolding system in terms of employing a single module, two, three and four modules in series. The white water is indicated to be much more advantageously processed, with only one or at most two modules in series in terms of both the capital and the operating cost categories.

Capital costs for the mill study are somewhat higher than provided in the original cost comparison provided in Table 104, but the operating charges range from 2 to 4 times higher. This is largely due to the much greater charge assigned to the module maintenance and membrane replacement costs at the $100 per module per year level.

There is much indication in recent studies of advantage arising from use of fewer modules in series, newer developments in membranes becoming available on the market, and use of higher velocities of flow rather than pulsing for fouling control. These factors have a principal effect on the increased operating charge.

Pressure pulsing of the entire module system by depressurizing at frequent intervals of each hour or so around the clock for months and years has been recognized as a severe test of module life performance. Much work directed to eliminating need for pulsing was reported in Section VIII of this report. Use of fewer modules and higher velocities greatly reduced or even eliminated need for pulsing. The optimization studies further confirmed that finding against use of pulsing. Confirmation trials in the mill are needed to prove these findings under practical plant operating conditions and are being planned.

The need for extending proven life performance of membrane modules in terms of freedom from irreversibly plugging by suspended matter

TABLE 105

SUPPLEMENTARY CAPITAL AND OPERATING CHARGE ESTIMATES

Mill Pilot Experience on NSSC White Water

No. of Modules in Series	Overall Average Flux Rate at 600 psig and 35°C, gfd	Total No. of Modules	Total Capital Cost, thousand dollars	Total Operating Cost, $/1000 gal. product water
1	8.3	887	231.3	3.79
2	7.4	985	235.0	4.06
3	6.6	1102	250.0	4.46
4	5.7	1284	277.8	5.08

Design capacity of RO unit = 144,000 gal./day of liquor
Initial concentration of the feed = 20 g/l feed rate
Final concentration of the feed = 100 g/l
Reference 5000 ppm sodium chloride solution
Flux rate at 600 psig and 35°C = 10.0 gfd
Module cost = $9.3 per sq ft of membrane
Module maintenance cost = $100 per module per year
Cost of electric power = 1.2 cents per Kwhr
Module depreciation = 5 years
Non-membrane equipment life = 5 years

and other materials during concentration processing, and even more importantly the extension of the life performance in terms of freedom from failures in the membrane support and in connecting seals is a primary goal in cost reduction for the RO process.

Practical applications for RO in the concentration processing of dilute pulp and paper manufacturing effluent streams await proving out of these substantial life performance criteria for the membrane modules.

SECTION XI

ACKNOWLEDGMENTS

The development of design factors for construction and installation of pilot and field demonstration units, the conduct of laboratory, pilot, and field studies, together with analytical work, engineering evaluations and report writing were performed by a single team. The project was initiated by the Pulp Manufacturers Research League and cooperating member pulp manufacturing corporations. The League merged into The Institute of Paper Chemistry, April 1, 1970, and its staff became the Effluent Processes Group within the Institute's Division of Industrial and Environmental Systems. Averill J. Wiley directed the project throughout.

Mr. J. M. Holderby, Consultant to the Research League, contributed actively to the supervision of field demonstrations as conducted by the staff field engineers; first by Mr. A. C. F. Ammerlaan and subsequently by Messrs. Kenneth Scharpf and I. K. Bansal. Mr. Bansal has contributed especially to the optimization studies and the computer program evaluations of process economics in Sections VIII, IX, and X. Mr. George Dubey, Research Associate, has supervised laboratory studies conducted throughout the project, and especially those described in Section V.

The conduct of a research and development project extending to five field demonstrations at different pulp and paper manufacturing facilities, has necessarily involved extensive and expert participation and cooperation of responsible individuals from each of those organizations.

The administration of the project was greatly facilitated by assistance of the Reverse Osmosis Subcommittee of the Research League under the Chairmanship of Mr. G. K. Dickerman, Technical Assistant to the President of Consolidated Papers, Inc., until his retirement in 1969, and subsequently of Mr. William R. Nelson, Director of Corporate Development for Green Bay Packaging Inc. The Subcommittee membership has also included the following:

Dr. Jack Jayne, Environmental Research Team, Corporate Research and Engineering, Kimberly-Clark Corporation, Neenah, Wisconsin

Mr. Francis C. Schroeder, Director, Environmental Control, Potlatch Forests, Inc., Northwest Paper Company, Cloquet, Minnesota

Mr. Donald Pryor, Manager, Environmental Control, Consolidated Papers, Inc., Wisconsin Rapids, Wisconsin

Mr. Milton A. Lefevre, Manager, Forest Chemical Products, Scott Paper Company, Oconto Falls, Wisconsin

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Mr. Donald Arps, Supervisor of Environmental Control,
Appleton Papers, Inc., Combined Locks, Wisconsin

The completeness of these studies has been made possible through the excellent cooperation of membrane and process equipment suppliers and of associated concerns developing specialized pumps and instrumentation in this new field of concentration processing of dilute industrial effluents. The following suppliers especially are to be commended for their cooperation, often at very great expense to their concerns and without charge to the project:

Membrane Equipment

Havens International and later Calgon Havens Division of Calgon Corporation

Gulf General Atomic Company and later Gulf Environmental Systems Company

Aerojet-General Corporation and later Envirogenics Company

Aqua-Chem, Inc.

American Standard Inc., Conseps Div., now Division of Abcor, Inc.

Westinghouse Electric Corporation

Osmonics, Inc.

Eastman Chemical Products, Inc., Subsidiary of Eastman Kodak Company

"Permasep" Products Division, E. I. du Pont de Nemours and Company

Supporting Equipment

Goulds Pumps, Inc. — Centrifugal pumps

A. W. Cash Valve Manufacturing Corporation — Back pressure control valves

Sweco, Inc. — Vibrating screens

Manton-Gaulin Manufacturing Company — Reciprocating pumps — Field unit

Milton Roy Company — Reciprocating pumps — Pilot scale

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Mr. Ralph H. Scott, Chief of Paper & Forest Industries, Environmental Protection Agency, as Federal Project Officer, has had responsibilities for immediate supervision of this project in accordance with objectives of the Federal Research and Demonstration Grant Program. Mr. George R. Webster, Water Quality Officer, and Mr. William J. Lacy, Chief, Industrial Pollution Control Branch, have also contributed substantially to the development and expediting of the Federal participation in this project. Their help and also that of their associates at EPA is acknowledged with sincere thanks.

SECTION XII

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SECTION XIII

PUBLICATIONS

The first paper in the following listing describes data obtained in an experimental program preliminary to designing the program for this Research and Demonstration Grant 12040 EEL. The following four papers were prepared and published on the basis of the data generated in the grant.

At least two additional technical papers are requested for future preparation and delivery based on the fourth field demonstration for RO processing of alkaline extraction kraft bleach effluents (see Section VII of this report) and on optimization of RO plant design (see Section IX).

1. Wiley, A. J., Ammerlaan, A. C. F., and Dubey, G. A. *Application of Reverse Osmosis to Processing of Spent Liquors from the Pulp and Paper Industry*. *Tappi*, *50*, no. 9: 455-60 (Sept., 1967).

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SECTION XIV

GLOSSARY

1. Alkaline extraction stage KBE — The caustic extraction effluents from the second and fourth stages of bleaching in the example of the CEDED sequence.

2. Bank/Stage — A group of modules connected externally in series, parallel or series/parallel arrangements comprising a separate concentration process.

3. BOD_5 — Biochemical oxygen demand based on the oxygen requirements of living organisms over a 5-day period while utilizing components of a waste stream for growth and/or reproduction.

4. Ca-base sulfite pulp — Produced by the calcium-base acid sulfite process.

5. Chemimechanical (CM) pulping process — A high yield process based on a short chemical cook followed by mechanical refining to separate the fibers in the softened chips.

6. Chlorination stage KBE — Some bleach sequences in multistage bleaching may chlorinate two or more times, but in this demonstration study it usually refers to the first chlorination stage as in CEDED (chlorination, caustic extraction, chlorine dioxide, caustic extraction, and a final stage of chlorine dioxide bleach).

7. COD — Chemical oxygen demand is the measurement of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by strong chemical oxidants (chromic acid).

8. Compaction — Decrease of water permeation rate with time at a fixed pressure.

9. Concentrate — The solution existing from the RO unit after removal of a portion of the water through the membrane.

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GLOSSARY (Cont'd.)

10. Condensates — The condensible products from the evaporative concentration of pulping liquors of the acid sulfite, bisulfite, NSSC and alkaline sulfate (kraft) processes.

11. Dynamic membrane — The formation of a layer on the surface of an intact membrane or other relatively impervious, but porous, surface which decreases the transport (increases the rejection) of solutes without markedly affecting the transport (flux rate) of the solvent.

12. Electrical resistance — A quantitative measure of the electrolytes present in a solution.

13. Fluo-solids — Fluid solids process of burning to obtain dry ash pellets.

14. Flux rate — Rate of permeation or transport of the solvent (water) through the membrane measured as gallons per square foot per day GF^2/D or simplified to gfd.

15. Fouling — Stoppage of fluid flow (permeation) through the membrane by a foreign material on the membrane surface or within the membrane matrix, as opposed to plugging which is a blockage of the flow of the process liquor along the module flow path.

16. Hydrolysis — Deacetylation of cellulose acetate membrane in a strong acidic or alkaline medium.

17. Inside diameter — Tubular RO systems in this study were of 0.5 inch I.D.

18. KBE — Kraft bleach effluents, an effluent of the various single stage or multistage methods of bleaching kraft pulp.

19. Kraft pulp — Pulp produced in alkaline sulfate (kraft) process of pulping.

20. Lignin — An amorphous polymeric substance related to cellulose that together with the cellulose forms the woody cell walls of plants and the cementing material between them.

GLOSSARY (Cont'd.)

21. Lignosulfonates — Compounds formed by the reaction of the bisulfite (HSO_3) ion and sulfurous acid in the cooking liquor with the lignin in the wood; present in the liquors as salts of the base used in pulping.

22. Membrane constant — Flux rate/effective driving pressure.

23. NH_3-base pulp — Produced by the ammonia-base acid sulfite process.

24. NSSC — Neutral sulfite-semichemical pulping, usually with sodium bisulfite but other bases such as ammonia are also used.

25. NSSC white water — Pulp wash water produced in "on-machine" washing of linerboard pulp.

26. Optical density — Measurement of light absorption of an appropriate dilution of the sample at 281 nm in a 1 cm square silica cell, and reported on basis of original, undiluted material.

27. Osmosis — Diffusion through a semipermeable membrane separating a solvent and a solution that tend to equalize their concentrations.

28. Osmotic pressure — The hydrostatic pressure required to stop the osmotic diffusion across a semipermeable membrane between two solutions of dissimilar concentrations.

29. Permeation resistance — (Osmotic pressure of the liquor) + (osmotic pressure increase due to concentration polarization and fouling).

30. Plugging — Stoppage of the flow of process liquor through the modules due to some foreign material, suspended solids, scale, precipitate, loose membrane in the flow path; as opposed to fouling which is a blockage of the flow of permeate through the membrane.

31. Pressate — Fluid from the Zenith screw press in the chemimechanical pulping process.

GLOSSARY (Cont'd.)

32. Pressure drop — The loss of pressure through a system due to friction losses in piping and modules, process stream velocity and viscosity.

33. Pressure pulse, hard — Rapid periodic and sharp reduction of the pressure from an operating level to atmospheric for the purpose of restoring the flux rate lost by the deposition of a fouling material on the membrane surface.

34. Pressure pulse, soft — Periodic slow reduction of the pressure from an operating level to atmospheric for the purpose of restoring the flux rate lost by the deposition of a fouling material on the membrane surface.

35. Pressure regulator — A spring or gas loaded, adjustable valve which can be used to set the pressure on the upstream solution under process.

36. Recovery ratio — The ratio of the quantity of a component (solids) in the concentrate to the quantity of the same component in the original feed.

37. Recycle ratio — The ratio of the quantity of the feed liquor recycled to the quantity of the liquor entering a recycling operation as fresh feed.

38. Reynolds number — A dimensionless number equalling (diameter of pipe x average linear velocity of the fluid x fluid density) ÷ fluid viscosity.

39. RO — Osmosis in reverse flow through a semipermeable membrane when external pressure in excess of the osmotic pressure is applied.

40. Semipermeable membranes — A membrane which is selective in that certain components in a solution (ordinarily the solvent) can pass through the membrane while one or more components cannot.

GLOSSARY (Cont'd.)

41. Spent liquor — Liquor separated from the pulp containing the residual cooking chemicals and dissolved constituents of the wood.

42. Stage/Bank — See Bank/Stage.

43. Sulfite pulp — Pulp produced by one of the various modifications of chemical and semichemical pulping with solutions of sulfite and bisulfites.

44. Temperature coefficient — The rate of change in the flux rate through a semipermeable membrane with changes in the temperature of the process stream.

45. Turbulent flow — A flow in a fluid in which the velocity at a given point varies erratically in magnitude and direction.

46. Velocity — Linear velocity of flow across the membrane surface.

SECTION XV

APPENDICES

Photographs, Fig. 64, 65, and 66.

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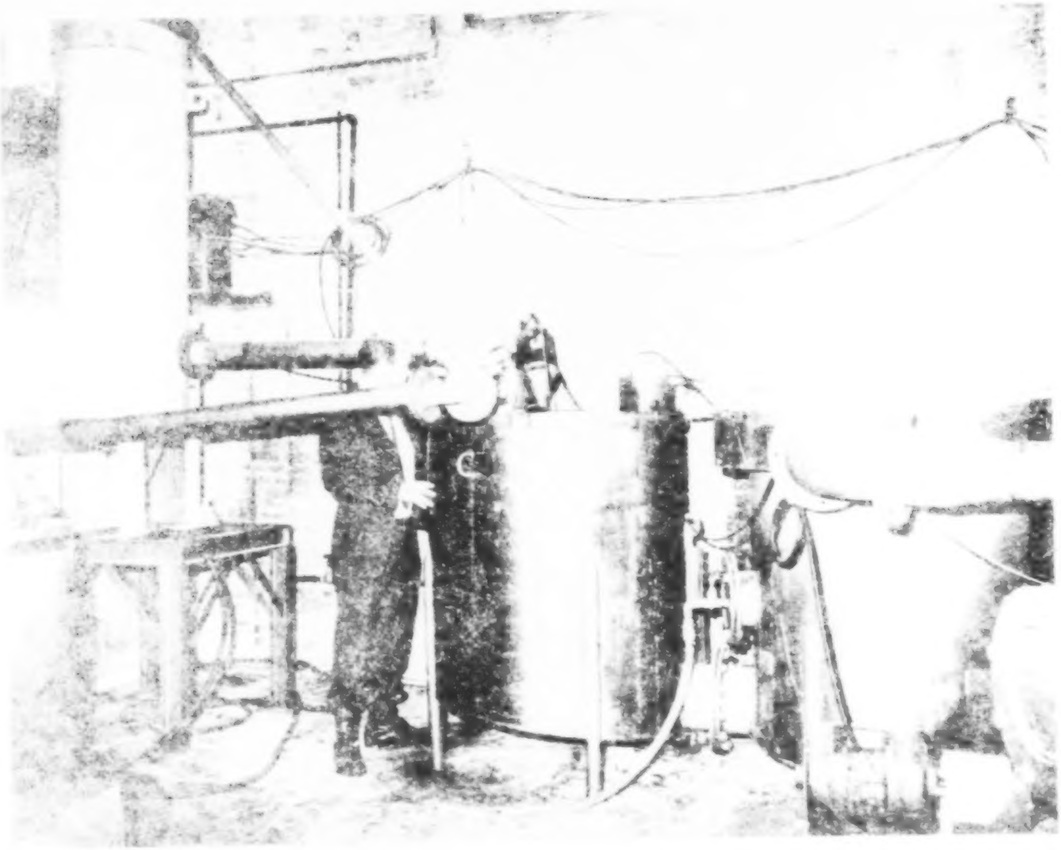

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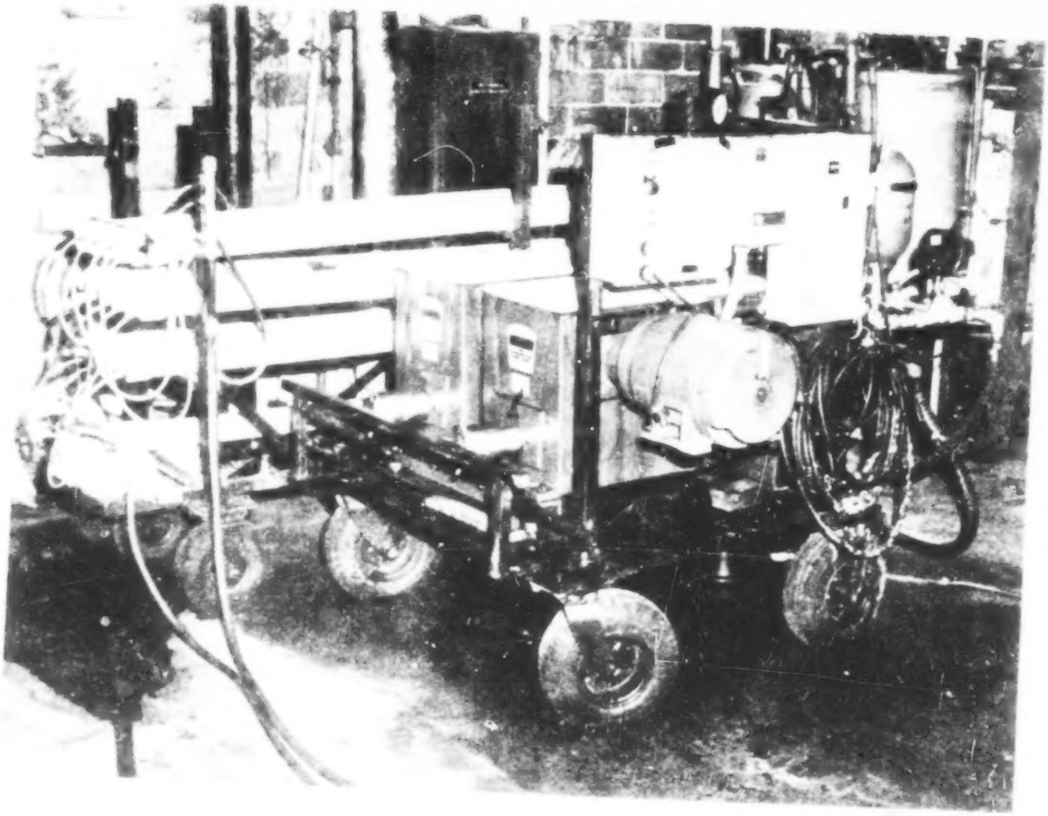

Figure 10. [illegible] Unit Operating in Pulp Mill to Process
Alkaline Extraction Stage Kraft Bleach Effluent.
Northwest Paper Company, Cloquet, Minnesota

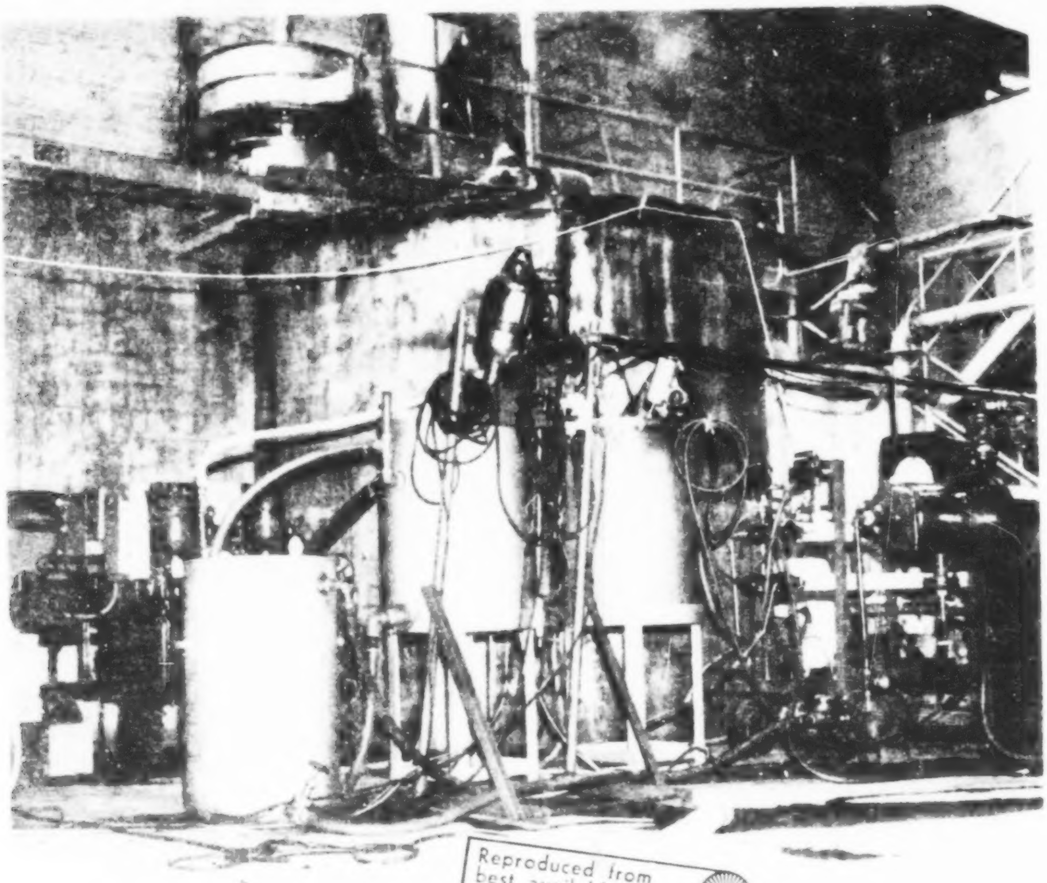

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Figure [illegible]. Photo of RO Pilot Installation Operating to Concentrate Dilute Chemimechanical Pulp Wash Water. Large 5000 Gallon Feed Tank in Center Background with Sweco Vibrating Screen and [illegible] Above. Pretreatment System in Foreground. [illegible] at Right. [illegible] Cooler [illegible] and [illegible] [illegible]

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5 *Organization*

Pulp Manufacturers Research League and The Institute of Paper Chemistry, Effluent Processes Group, Division of Industrial and Environmental Systems

6 *Title*

Reverse Osmosis Concentration of Dilute Pulp and Paper Effluents

10 *Author(s)*

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*Reverse Osmosis, *Pulp Wastes, *Waste Treatment, Water Reuse, Chemical Recovery, Economic Feasibility, Technical Feasibility, Membrane Fouling.

25 *Identifiers (Starred First)*

*Waste Water Treatment, *Industrial Wastes, *Semipermeable Membranes, Separation Techniques, Desalination, Water Costs, Membrane Cleaning.

27 *Abstract*

Adaptation of reverse osmosis as a method of concentration for dilute effluents of pulping, bleaching, and paper manufacture was conducted in laboratory, pilot scale, and in large 50,000 gallon per day field demonstrations at pulp mills. Most of these dilute wastes at 1 percent solids contained suspended particles, colloidal suspensoids, large molecular-weight wood derived organics, and/or scale-forming inorganic chemical residues. Tubular membrane systems capable of being operated at self-cleaning velocities increasing beyond 2.0 feet per second, as concentration advanced to 10 percent solids, were apparently best adapted to processing these effluents at sustained high flux rates and relatively free of fouling problems. Capillary fiber and spiral wound sheet membrane systems required expensive clarification treatment before and during concentration. Tubular systems studied were subject to excessive failure rates in terms of life of membrane support structures or to leakage of internal connections based on the support structure. Feasibility of employing RO for concentration of dilute pulping and bleaching effluents depends on developing routes to substantial improvement in life expectancy of RO equipment to maintain high flux rates and rejections at much lower membrane maintenance and replacement costs than prevailed with equipment available for these studies conducted from 1967 through 1971.

Abstractor

Institution

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